Electronic Supplementary Material (ESI) for Organic .
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Supplementary Information

For

Diastereoselective formation of aziridines from diazocarbonyl compounds and N-(O-pivaloylated D-galactosyl) benzylideneamines and ring-opening reactions with p-toluenethiol

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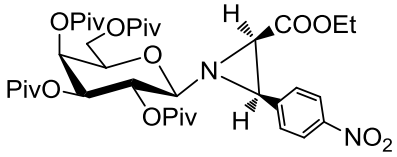
General Remarks

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) using commercial silica gel HSGF254 plates. Column chromatography was performed on Silica Gel 60 (E. Merck, 230-400 mesh). The ^{1}H (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded with Bruker AM-400 spectrometer in $CDCl_3$ solution. Chemical shifts were referenced with tetramethylsilane (0 ppm for ^{1}H and 77.0 ppm for ^{13}C). The HR-ESI-MS data were measured on a Bruker Apex IV FTMS. The chiral HPLC data of **3** were measured by Daicel Chiralcel OD-H, and the data of **4** were measured by Daicel Chiralpak IB.

General procedure for the preparation of 3

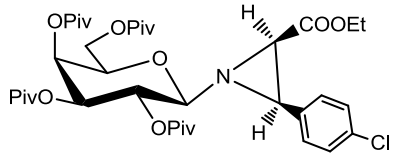
An oven-dried 10 mL vial was charged with **1** (0.30 mmol), then 3 mL of dry CH_2Cl_2 and $BF_3{\cdot}OEt_2$ (0.15 mmol) were added. The mixture solution was stirred at -40℃ for 15 min before the addition of **2** (0.45 mmol) via a syringe. The resulting solution was continued stirring until the reaction was complete as shown by TLC (usually 2 hours). Then three drops of triethylamine were added and the mixture was gradually warmed to room temperature. The mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate=15/1), yielding the corresponding compounds **3** as white or pale yellow solid.

cis-1-(2,3,4,6-tetra-O-pivaloyl-β-D-galactosyl)-(3*S*)-(4-nitrophenyl)-aziridine-(2*R*)-ethyl formate (3a)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.2 Hz, 2H, *H*-Ar), 7.56 (d, *J* = 8.0 Hz, 2H, *H*-Ar), 5.43 (d, *J* = 3.0 Hz, 1H, *H*-4), 5.33 (t, *J* = 9.6 Hz, 1H, *H*-2), 5.20 (dd, *J* = 10.5, 3.0 Hz, 1H, *H*-3), 4.54 (d, *J* = 8.8 Hz, 1H, *H*-1), 4.24 – 4.09 (m, 1H, *H*-5), 4.08 – 3.81 (m, 4H, *H*-6, -C*H*$_2$CH$_3$), 3.73 (d, *J* = 6.5 Hz, 1H, -C*H*COO-), 3.27 (d, *J* = 6.5 Hz, 1H, -C*H*-Ar), 1.29 (s, 9H, *H*-Piv), 1.24 (s, 9H, *H*-Piv), 1.19 (s, 9H, *H*-Piv), 1.13 (s, 9H, *H*-Piv), 1.02 (t, *J* = 7.0 Hz, 3H, -C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.78, 177.27, 176.66, 176.52, 166.67, 147.38, 141.99, 128.96, 122.95, 86.49, 72.45, 71.12, 67.72, 66.84, 61.04, 60.86, 40.47, 39.11, 38.73, 38.29, 27.21, 27.05, 13.96. **HR-ESI-MS**: Calcd for $C_{37}H_{55}N_2O_{13}$ $[M+H]^+$: 735.3699, found: 735.3700.

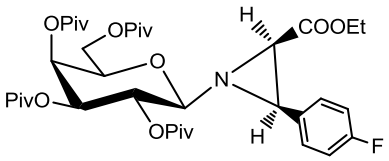
cis-1-(2,3,4,6-tetra-O-pivaloyl-β-D-galactosyl)-(3*S*)-(4-chlorophenyl)-aziridine-(2*R*)-ethyl formate (3b)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 6.8 Hz, 2H, *H*-Ar), 7.26 (d, *J* = 8.5 Hz, 2H, *H*-Ar), 5.44 (d, *J* = 3.1 Hz, 1H, *H*-4), 5.33 (dd, *J* = 10.4, 8.9 Hz, 1H, *H*-2), 5.20 (dd, *J* = 10.4, 3.2 Hz, 1H, *H*-3), 4.48 (d, *J* = 8.8 Hz, 1H, *H*-1), 4.23 – 4.08 (m, 1H, *H*-5), 4.08 – 3.81 (m, 4H, *H*-6, -C*H*$_2$CH$_3$), 3.66 (d, *J* = 6.7 Hz, 1H, -C*H*COO-), 3.19 (d, *J* = 6.7 Hz, 1H, -C*H*-Ar), 1.29 (s, 9H, *H*-Piv), 1.23 (s, 9H, *H*-Piv), 1.19 (s, 9H, *H*-Piv), 1.13 (s, 9H, *H*-Piv), 1.02 (t, *J* = 7.0 Hz, 3H, -C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.83, 177.33, 176.76, 176.51, 167.13, 133.37, 133.00, 129.38, 127.92, 86.84, 72.36, 71.27, 67.83, 66.93, 61.15, 60.64, 40.62, 39.13, 38.78, 38.75, 38.73, 38.18, 27.24, 27.08, 13.98. **HR-ESI-MS**: Calcd for $C_{37}H_{55}ClNO_{11}$ $[M+H]^+$: 724.3458, found:

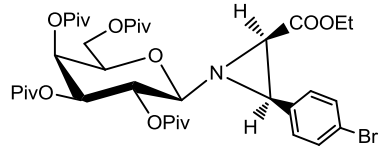
724.3447.

***cis*-1-(2,3,4,6-tetra-O-pivaloyl-β-D-galactosyl)-(3*S*)-(4-fluorophenyl)-aziridine-(2*R*)-ethyl formate (3c)**



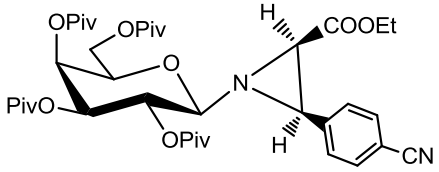
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, 2H, *H*-Ar), 6.97 (t, *J* = 8.6 Hz, 2H, *H*-Ar), 5.43 (d, *J* = 3.0 Hz, 1H, *H*-4), 5.33 (t, *J* = 9.6 Hz, 1H, *H*-2), 5.20 (dd, *J* = 10.4, 2.8 Hz, 1H, *H*-3), 4.47 (d, *J* = 8.8 Hz, 1H, *H*-1), 4.16 (m, 1H, *H*-5), 4.07 – 3.80 (m, 4H, *H*-6, -CH_2CH$_3$), 3.65 (d, *J* = 6.6 Hz, 1H, -C*H*COO-), 3.17 (d, *J* = 6.6 Hz, 1H, -C*H*-Ar), 1.31 (s, 9H, *H*-Piv), 1.23 (s, 9H, *H*-Piv), 1.20 (s, 9H, *H*-Piv), 1.14 (s, 9H, *H*-Piv), 1.01 (t, *J* = 7.1 Hz, 3H, -CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.79, 177.31, 176.74, 176.46, 167.19, 130.13, 129.62, 129.54, 114.72, 114.51, 86.97, 72.37, 71.32, 67.86, 66.95, 61.17, 60.53, 40.61, 39.12, 38.76, 38.73, 38.71, 38.18, 27.22, 27.07, 13.94. **HR-ESI-MS**: Calcd for $C_{37}H_{55}FNO_{11}$ $[M+H]^+$: 708.3753, found: 708.3762.

***cis*-1-(2,3,4,6-tetra-O-pivaloyl-β-D-galactosyl)-(3*S*)-(4-bromophenyl)-aziridine-(2*R*)-ethyl formate (3d)**



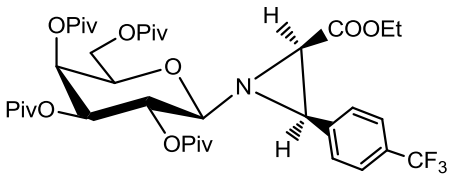
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, 2H, *H*-Ar), 7.26 (d, 2H, *H*-Ar), 5.42 (d, *J* = 3.1 Hz, 1H, *H*-4), 5.31 (dd, *J* = 10.4, 8.8 Hz, 1H, *H*-2), 5.18 (dd, *J* = 10.4, 3.2 Hz, 1H, *H*-3), 4.47 (d, *J* = 8.8 Hz, 1H, *H*-1), 4.21 – 4.07 (m, 1H, *H*-5), 4.07 – 3.78 (m, 4H, *H*-6, -CH_2CH$_3$), 3.61 (d, *J* = 6.7 Hz, 1H, -C*H*COO-), 3.18 (d, *J* = 6.7 Hz, 1H, -C*H*-Ar), 1.29 (s, 9H, *H*-Piv), 1.22 (s, 9H, *H*-Piv), 1.19 (s, 9H, *H*-Piv), 1.12 (s, 9H, *H*-Piv), 1.01 (t, *J* = 7.1 Hz, 3H, -CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.79, 177.30, 176.73, 176.48, 167.07, 133.55, 130.85, 129.72, 121.53, 86.83, 72.40, 71.29, 67.83, 66.94, 61.15, 60.62, 40.66, 39.12, 38.77, 38.73, 38.72, 38.12, 27.23, 27.07, 13.96. **HR-ESI-MS**: Calcd for $C_{37}H_{55}BrNO_{11}$ $[M+H]^+$: 768.2953, found: 768.2967.

***cis*-1-(2,3,4,6-tetra-O-pivaloyl-β-D-galactosyl)-(3*S*)-(4-cyanophenyl)-aziridine-(2*R*)-ethyl formate (3e)**



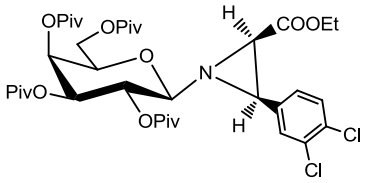
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, 2H, *H*-Ar), 7.51 (d, 2H, *H*-Ar), 5.43 (d, *J* = 3.1 Hz, 1H, *H*-4), 5.32 (dd, *J* = 10.4, 8.9 Hz, 1H, *H*-2), 5.19 (dd, *J* = 10.4, 3.1 Hz, 1H, *H*-3), 4.50 (d, *J* = 8.8 Hz, 1H, *H*-1), 4.17 (m, 1H, *H*-5), 4.07 – 3.80 (m, 4H, *H*-6, -CH_2CH$_3$), 3.70 (d, *J* = 6.7 Hz, 1H, -C*H*COO-), 3.24 (d, *J* = 6.7 Hz, 1H, -C*H*-Ar), 1.30 (s, 9H, *H*-Piv), 1.24 (s, 9H, *H*-Piv), 1.18 (s, 9H, *H*-Piv), 1.12 (s, 9H, *H*-Piv), 1.00 (t, *J* = 7.1 Hz, 3H, -CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.78, 177.28, 176.67, 176.50, 166.73, 140.01, 131.53, 128.86, 118.77, 111.37, 86.62, 72.47, 71.17, 67.77, 66.88, 61.08, 60.80, 40.69, 39.12, 38.77, 38.73, 38.31, 27.22, 27.06, 13.94. **HR-ESI-MS**: Calcd for $C_{38}H_{55}N_2O_{11}$ $[M+H]^+$: 715.3800, found: 715.3806.

***cis*-1-(2,3,4,6-tetra-O-pivaloyl-β-D-galactosyl)-(3*S*)-(4-trifluoromethylphenyl)-aziridine-(2*R*)-ethyl formate (3f)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.7 Hz, 2H, *H*-Ar), 7.50 (d, *J* = 8.7 Hz, 2H, *H*-Ar), 5.43 (d, *J* = 3.1 Hz, 1H, *H*-4), 5.32 (dd, *J* = 10.4, 8.9 Hz, 1H, *H*-2), 5.20 (dd, *J* = 10.4, 3.2 Hz, 1H, *H*-3), 4.51 (d, *J* = 8.8 Hz, 1H, *H*-1), 4.22 – 4.08 (m, 1H, *H*-5), 4.07 – 3.79 (m, 4H, *H*-6, -CH_2CH$_3$), 3.71 (d, *J* = 6.7 Hz, 1H, -C*H*COO-), 3.23 (d, *J* = 6.7 Hz, 1H, -C*H*-Ar), 1.30 (s, 9H, *H*-Piv), 1.23 (s, 9H, *H*-Piv), 1.19 (s, 9H, *H*-Piv), 1.12 (s, 9H, *H*-Piv), 0.98 (t, *J* = 7.1 Hz, 3H, -CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.80, 177.30, 176.71, 176.51, 166.94, 138.55, 128.38, 124.67, 124.63, 86.67, 72.38, 71.19, 67.78, 66.89, 61.11, 60.68, 40.64, 39.11, 38.76, 38.72, 38.18, 27.21, 27.05, 13.85. **HR-ESI-MS**: Calcd for $C_{38}H_{55}F_3NO_{11}$ $[M+H]^+$: 758.3721, found: 758.3722.

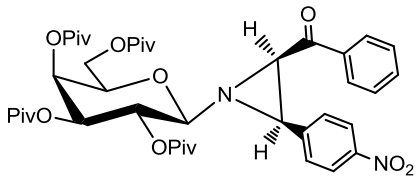
***cis*-1-(2,3,4,6-tetra-O-pivaloyl-β-D-galactosyl)-(3*S*)-(3,4-dichlorophenyl)-aziridine-(2*R*)-ethyl formate (3j)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, 1H, *H*-Ar), 7.34 (d, 1H, *H*-Ar), 7.20 (dd, *J* = 8.3, 1.9 Hz, 1H, *H*-Ar), 5.40 (d, *J* = 3.1 Hz, 1H, *H*-4), 5.34 – 5.24 (m, 1H, *H*-2), 5.23 – 5.14 (m, 1H, *H*-3), 4.49 (d, *J* = 8.9 Hz, 1H, *H*-1), 4.13 (m, 1H, *H*-5), 4.08 – 3.84 (m, 4H, *H*-6, -CH_2CH$_3$), 3.60 (d, *J* = 6.6 Hz, 1H, -C*H*COO-), 3.20 (d, *J* = 6.7 Hz, 1H, -C*H*-Ar), 1.29 (s, 9H, *H*-Piv), 1.25 (s, 9H, *H*-Piv), 1.19 (s, 9H, *H*-Piv), 1.13 (s, 9H, *H*-Piv), 1.05 (t, *J* = 7.1 Hz, 3H, -CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.79, 177.28, 176.70, 176.50, 166.98, 134.81, 131.87, 131.52, 130.21, 129.73, 127.34, 86.47, 72.38, 71.19, 67.75, 66.85, 61.06, 60.77, 39.95, 39.11, 38.76, 38.74, 38.73, 38.13, 27.22,

27.06, 13.96. **HR-ESI-MS**: Calcd for $C_{37}H_{54}Cl_2NO_{11}$ $[M+H]^+$: 758.3068, found: 758.3081.

***cis*-1-(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactosyl)-(2R)-benzoyl-(3S)-(4-nitrophenyl)-aziridine (3k)**

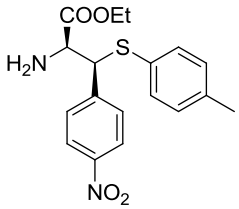


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.7 Hz, 2H, *H*-p-NO_2-Ph), 8.03 (d, 2H, *H*-p-NO_2-Ph), 7.62 (t, *J* = 7.4 Hz, 1H, *H*-Ph), 7.58 – 7.46 (m, 4H, *H*-Ph), 5.64 (dd, *J* = 2.7, 3.1 Hz, 1H, *H*-4), 5.36 (d, *J* = 10.4, 8.9 Hz, 1H, *H*-2), 5.21 – 5.06 (m, 1H, *H*-3), 4.31 (d, *J* = 8.9 Hz, 1H, *H*-1), 3.91 (d, *J* = 2.7 Hz, 1H, *H*-5), 3.86 – 3.68 (m, 2H, *H*-6), 3.57 (d, *J* = 2.8 Hz, 1H, -C*H*CO-), 3.39 (dd, *J* = 10.5, 5.4 Hz, 1H, -C*H*-Ar), 1.28 (s, 9H, *H*-Piv), 1.10 (s, 9H, *H*-Piv), 0.99 (s, 9H, *H*-Piv), 0.81 (s, 9H, *H*-Piv). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.32, 177.57, 177.33, 176.74, 176.22, 147.55, 144.38, 137.38, 133.90, 128.81, 128.58, 127.49, 123.76, 88.37, 72.52, 71.54, 70.11, 66.63, 60.15, 47.19, 45.53, 39.04, 38.76, 38.56, 38.47, 27.18, 27.11, 26.87, 26.83. **HR-ESI-MS**: Calcd for $C_{41}H_{55}N_2O_{12}$ $[M+H]^+$: 767.3749, found: 767.3750.

General procedure for the preparation of 4

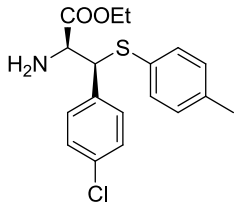
An oven-dried 10 mL vial was charged with **3** (0.15 mmol) and 4-methylbenzenethiol (0.30 mmol). After the solid was dissolved by 2.5 mL of dry CH_2Cl_2, $BF_3{\cdot}OEt_2$ (0.20 mmol) was added. Then the solution was stirred at room temperature for 7 days. When the reaction was complete as shown by TLC, triethylamine (0.20 mmol) was added to adjust the PH, decreasing the salt form of amino acids. The mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1), yielding the corresponding β-S-substituted phenylalanine derivatives **4** as yellow viscous oil.

ethyl-(2S,3S)-2-amino-3-(4-methoxyphenylthiol)-3-(4-nitrophenyl)-propanoate (4a)



^{1}H NMR (400 MHz, CD_3OD) δ 8.12 (d, *J* = 8.6 Hz, 2H, *H*-p-NO_2-Ph), 7.54 (d, *J* = 8.6 Hz, 2H, *H*-p-NO_2-Ph), 7.19 (d, *J* = 7.8 Hz, 2H, *H*-p-CH_3-Ph), 7.06 (d, *J* = 7.8 Hz, 2H, *H*-p-CH_3-Ph), 4.60 (d, *J* = 7.2 Hz, 1H, -C*H*-NH_2), 4.03-3.95 (m, 2H, -C$H_2$$CH_3$), 3.91 (d, *J* = 7.2 Hz, 1H, -C*H*-S-), 2.27 (s, 3H, -CH_3), 1.06 (t, *J* = 7.0 Hz, 3H, -CH_2CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.46(CO), 148.67(Ar), 148.58(Ar), 139.71(Ar), 134.66(Ar), 130.96(Ar), 130.90(Ar), 130.62(Ar), 124.26(Ar), 62.39(-*C*H-NH_2), 60.01 (2, -*C*$H_2$$CH_3$, -*C*H-S-), 21.11(-*C*$H_3$), 14.25(-$CH_2$*C*$H_3$). **HR-ESI-MS**: Calcd for $C_{18}H_{20}N_2O_4S$ $[M+H]^+$: 361.1216, found: 361.1210. $[\alpha]_D^{20} = 120°$ (*c* 0.5g/100mL in CH_3OH).

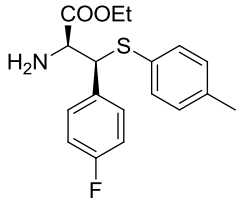
ethyl-(2S,3S)-2-amino-3-(4-methoxyphenylthiol)-3-(4-chlorophenyl)-propanoate (4b)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.0 Hz, 2H, *H*-p-Cl-Ph), 7.24 (d, *J* = 8.0 Hz, 2H, *H*-p-Cl-Ph), 7.15 (d, *J* = 8.0 Hz, 2H, *H*-p-CH_3-Ph), 7.01 (d, *J* = 8.0 Hz, 2H, *H*-p-CH_3-Ph), 4.43 (d, *J* = 6.0 Hz, 1H, -C*H*-NH_2), 4.06-3.92 (m, 2H, -C$H_2$$CH_3$), 3.80 (d, *J* = 6.0 Hz, 1H, -C*H*-S-), 2.28 (s, 3H, -CH_3), 1.08 (t, *J* = 6.8 Hz, 3H, -CH_2CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.01(CO), 137.95(2, Ar), 133.32(Ar), 133.17(Ar), 129.88(Ar), 129.79(Ar), 129.71(Ar), 128.44(Ar), 61.30(-*C*H-NH_2), 59.62(-*C*$H_2$$CH_3$),

58.99(-*C*H-S-), 21.09(-*C*H_3), 13.92(-CH_2*C*H_3). **HR-ESI-MS**: Calcd for $C_{18}H_{20}ClNO_2S$ $[M+H]^+$: 350.0976, found: 350.0972; $[M+Na]^+$:372.0796, found: 372.0801. $[\alpha]_D^{20} = 140°$ (c 0.5g/100mL in CH_3OH).

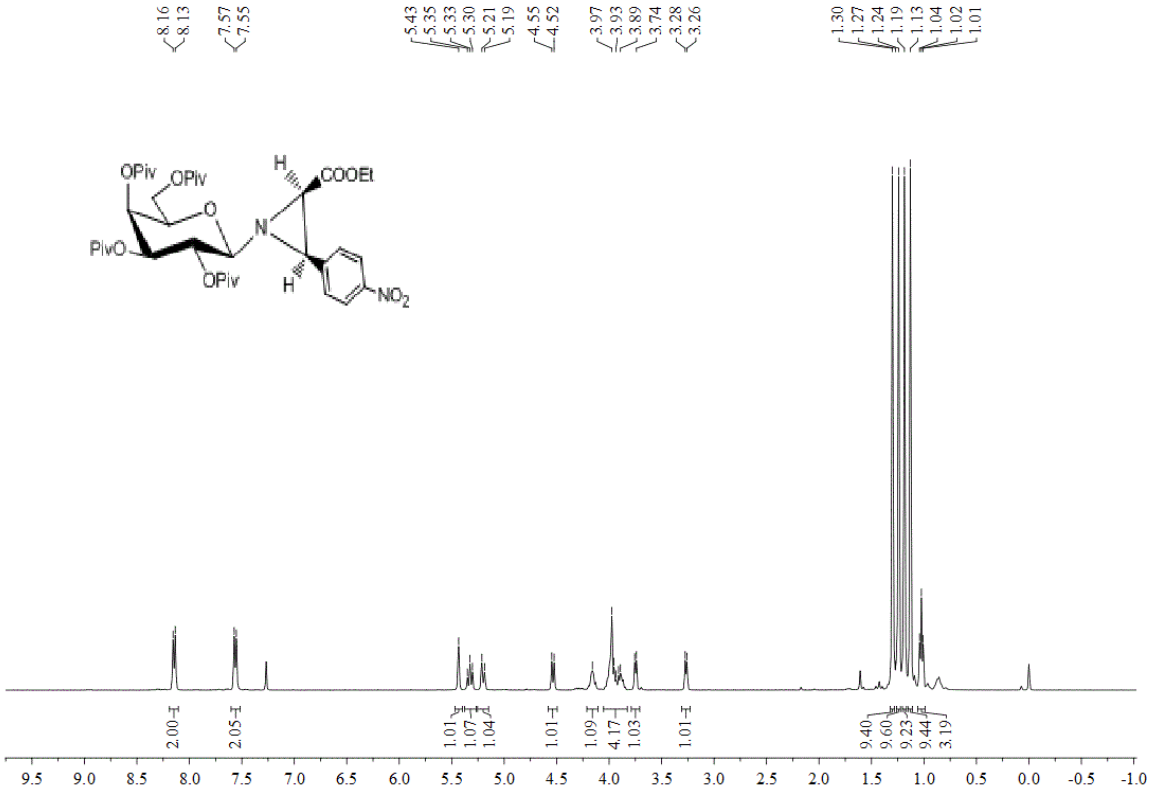
ethyl-(2S,3S)-2-amino-3-(4-methoxyphenylthiol)-3-(4-fluorophenyl)-propanoate (4c)

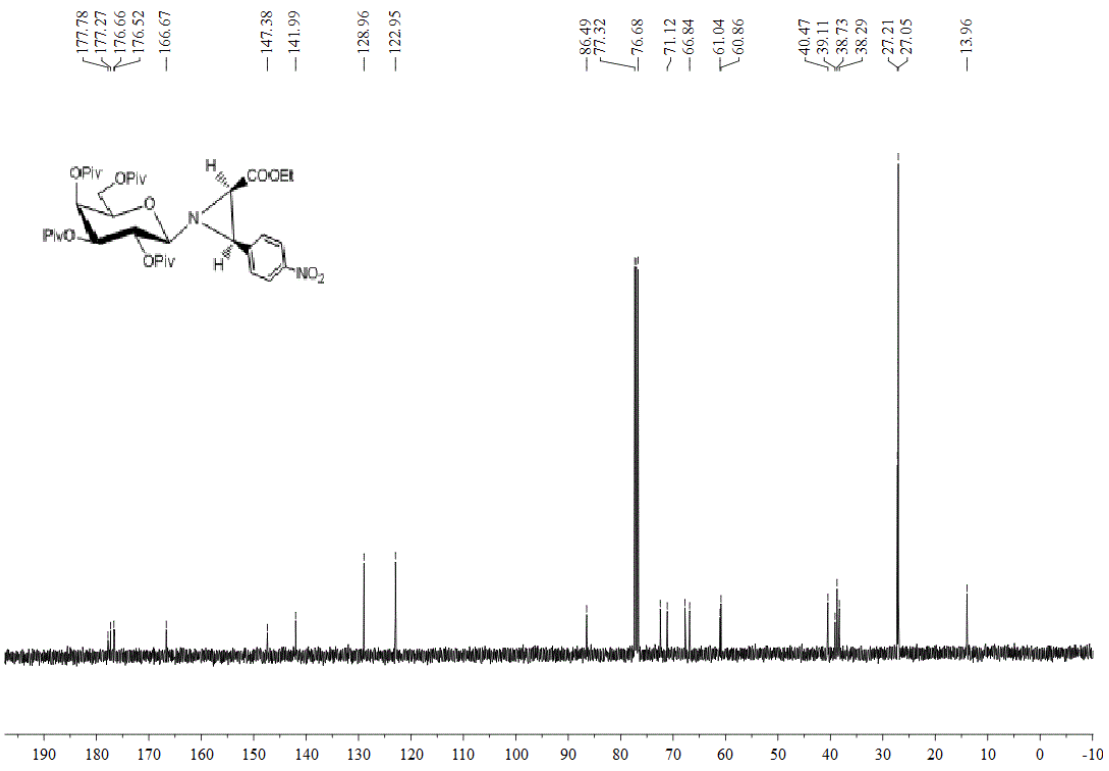


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H, *H*-p-F-Ph), 7.15 (d, *J* = 8.0 Hz, 2H, *H*-p-CH_3-Ph), 7.01 (d, *J* = 8.0 Hz, 2H, *H*-p-CH_3-Ph), 6.98-6.93 (m, 2H, *H*-p-F-Ph), 4.44 (d, *J* = 6.0 Hz, 1H, -C*H*-NH_2), 4.04-3.91 (m, 2H, -C*H*$_2$$CH_3$), 3.80 (d, *J* = 6.0 Hz, 1H, -C*H*-S-), 2.28 (s, 3H, -C*H*$_3$), 1.07 (t, *J* = 8.0 Hz, 3H, -CH_2C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.32(CO), 137.88(Ar), 135.43(Ar), 133.20(Ar), 130.08(Ar), 130.00(Ar), 129.67(Ar), 115.25(Ar), 115.03(Ar), 61.22(-*C*H-NH_2), 59.84(-*C*$H_2$$CH_3$), 58.94(-*C*H-S-), 21.08(-*C*H_3), 13.91(-CH_2*C*H_3). **HR-ESI-MS**: Calcd for $C_{18}H_{20}FNO_2S$ $[M+H]^+$: 334.1277, found: 334.1272. $[\alpha]_D^{20} = 130°$ (c 0.5g/100mL in CH_3OH).

Copies of NMR spectra of 3 and 4

3a





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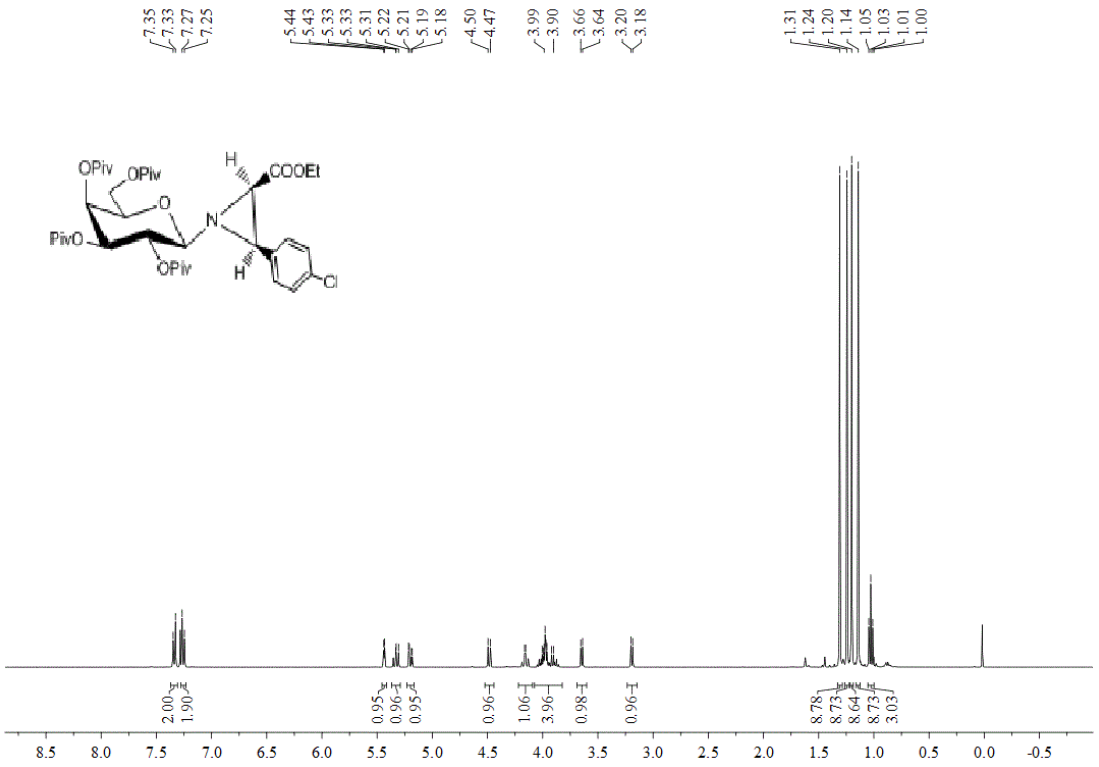
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4.50
4.47
3.99
3.90
3.66
3.64
3.20
3.18
1.31
1.24
1.20
1.14
1.05
1.03
1.01
1.00
OPiv
OPiv
O
PivO
OPiv
N
H
COOEt
H
Cl
2.00
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0.96
0.95
0.96
1.06
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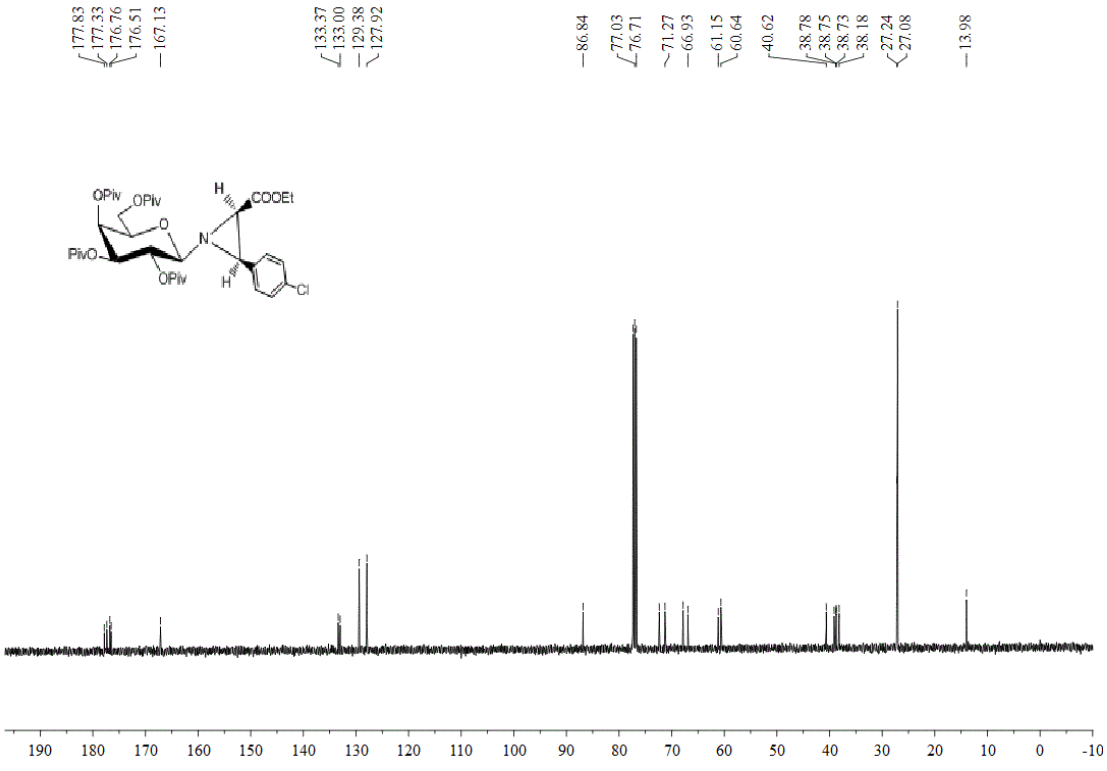
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OPiv
OPiv
O
PivO
OPiv
N
H
COOEt
H
Cl
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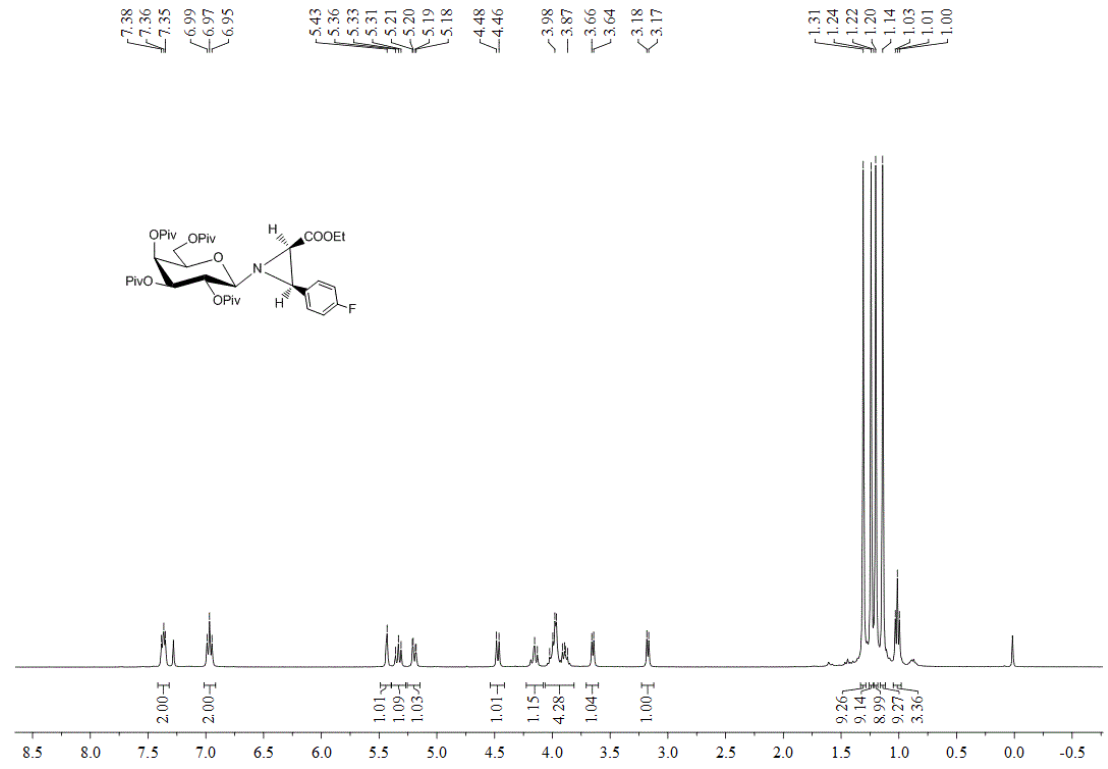
3c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1.24
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1.20
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H
F
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7.0
6.5
6.0
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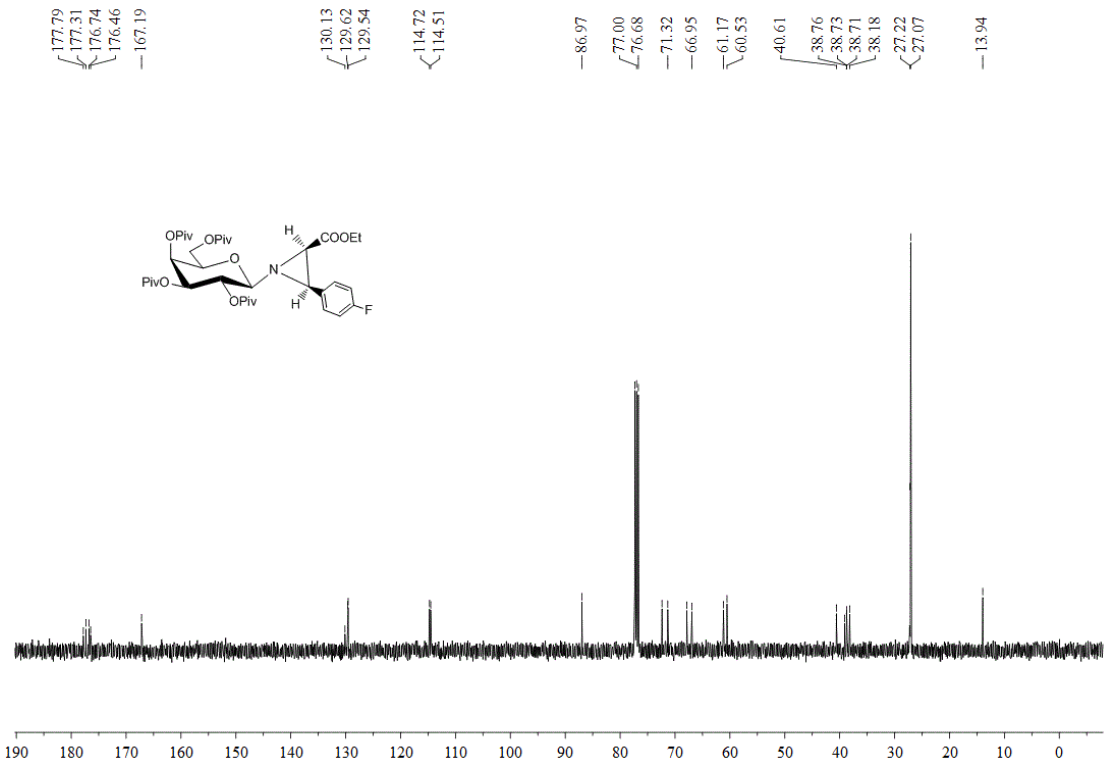
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38.71
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27.22
27.07
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H
COOEt
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F
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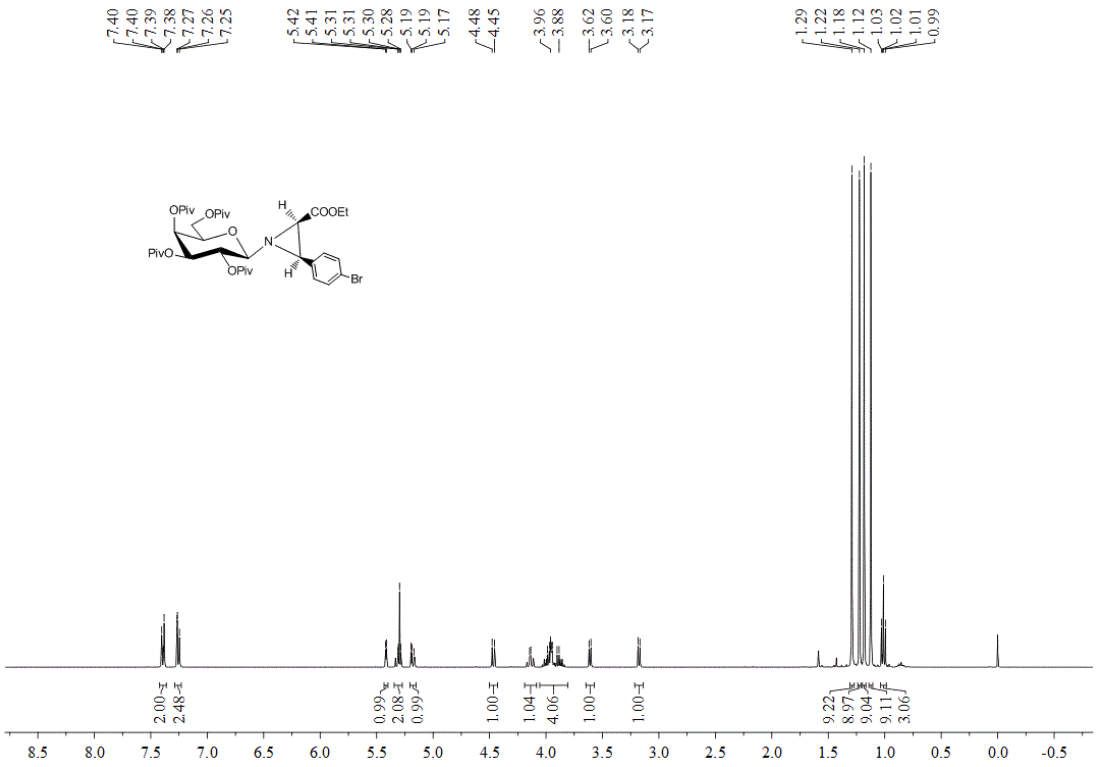
3d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5.19
5.19
5.17
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1.12
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COOEt
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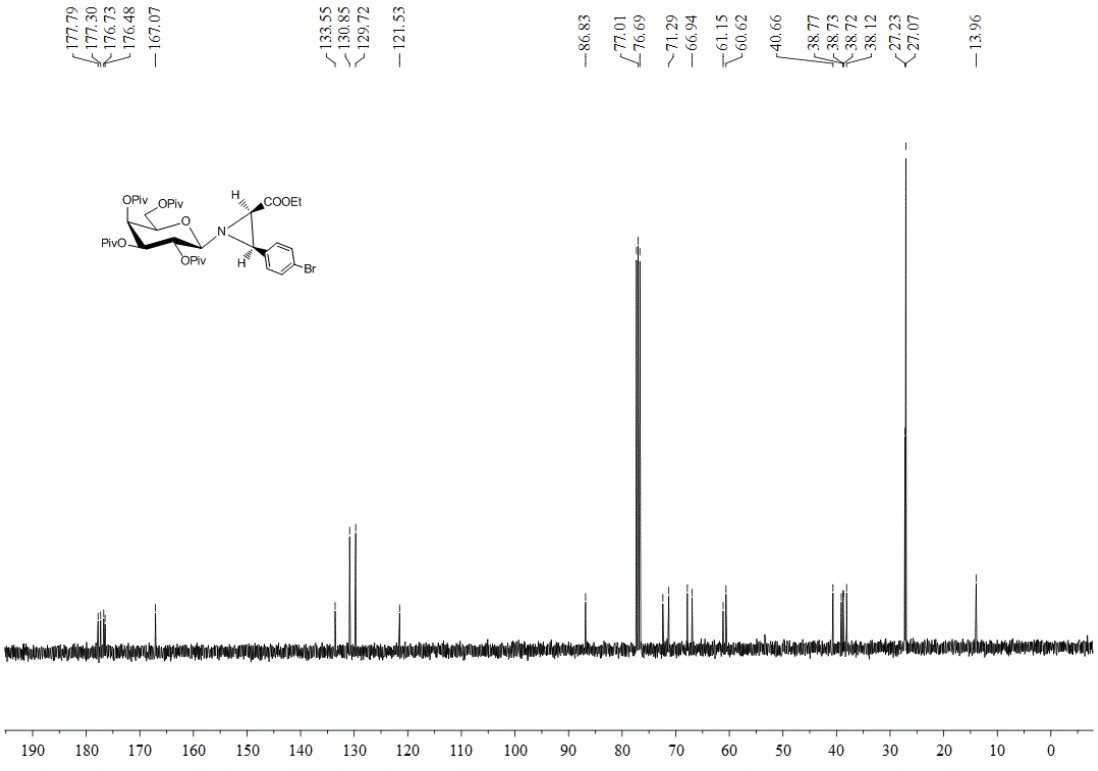
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66.94
61.15
60.62
40.66
38.77
38.73
38.72
38.12
27.23
27.07
13.96
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OPiv
O
N
PivO
OPiv
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COOEt
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Br
190
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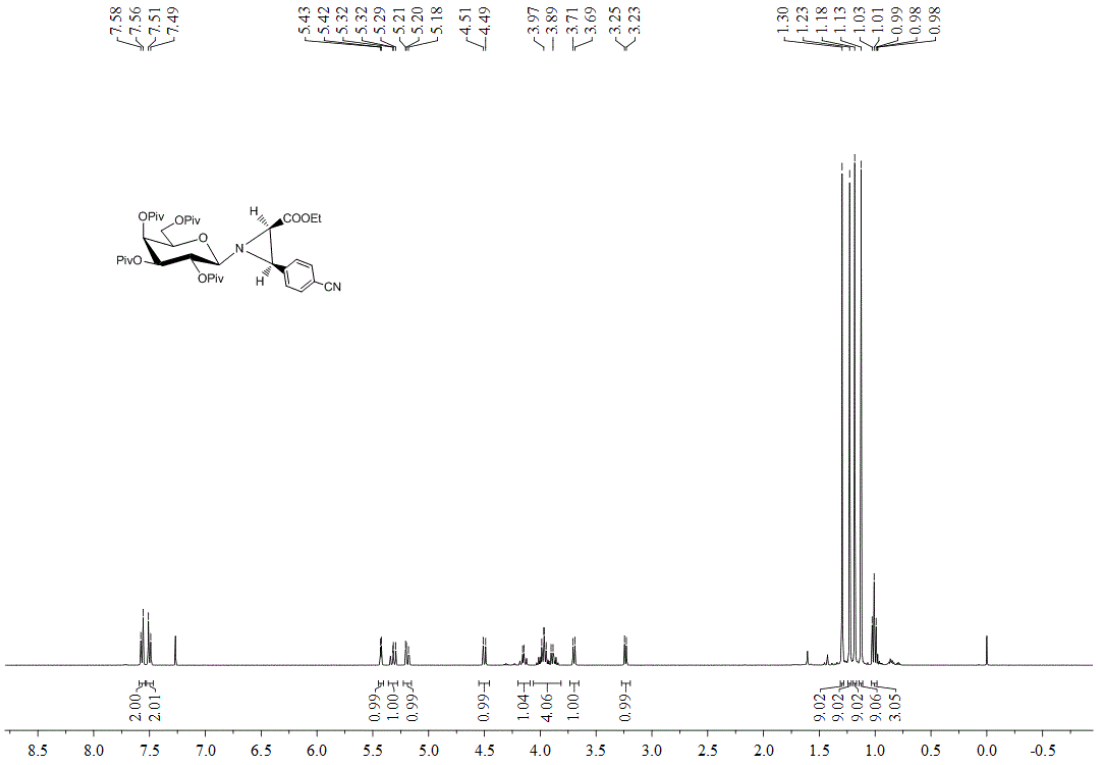
3e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3.25
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1.23
1.18
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CN
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0.99
1.04
4.06
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9.06
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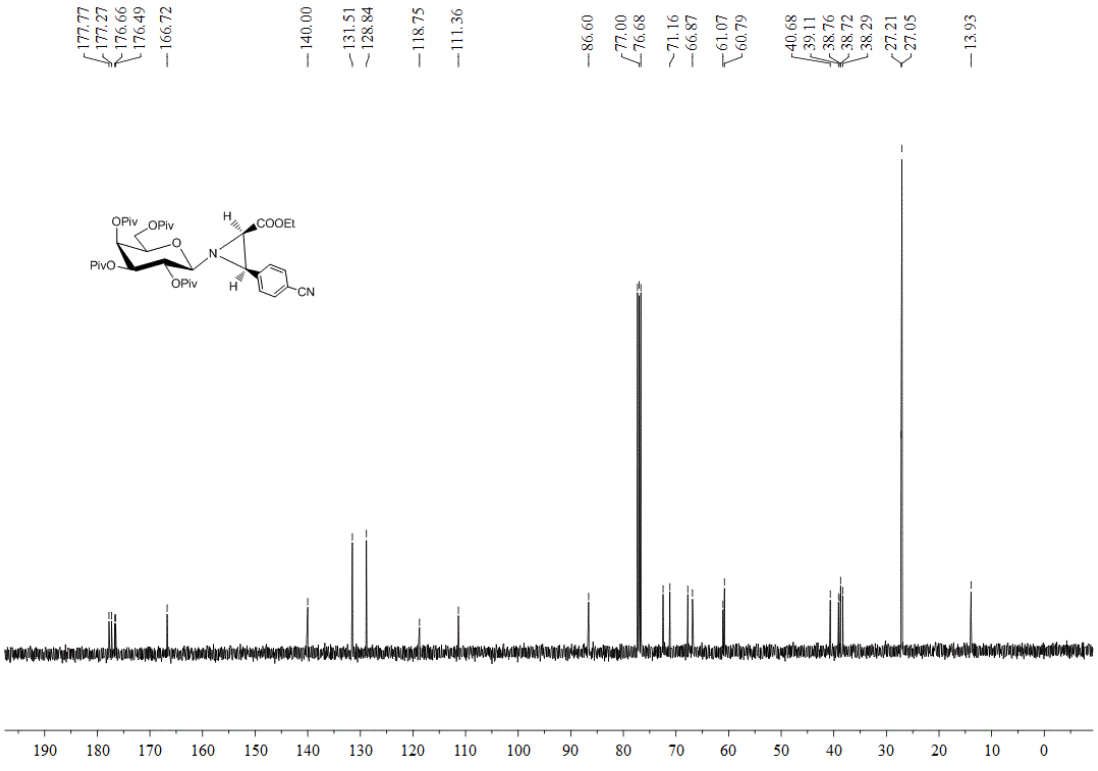
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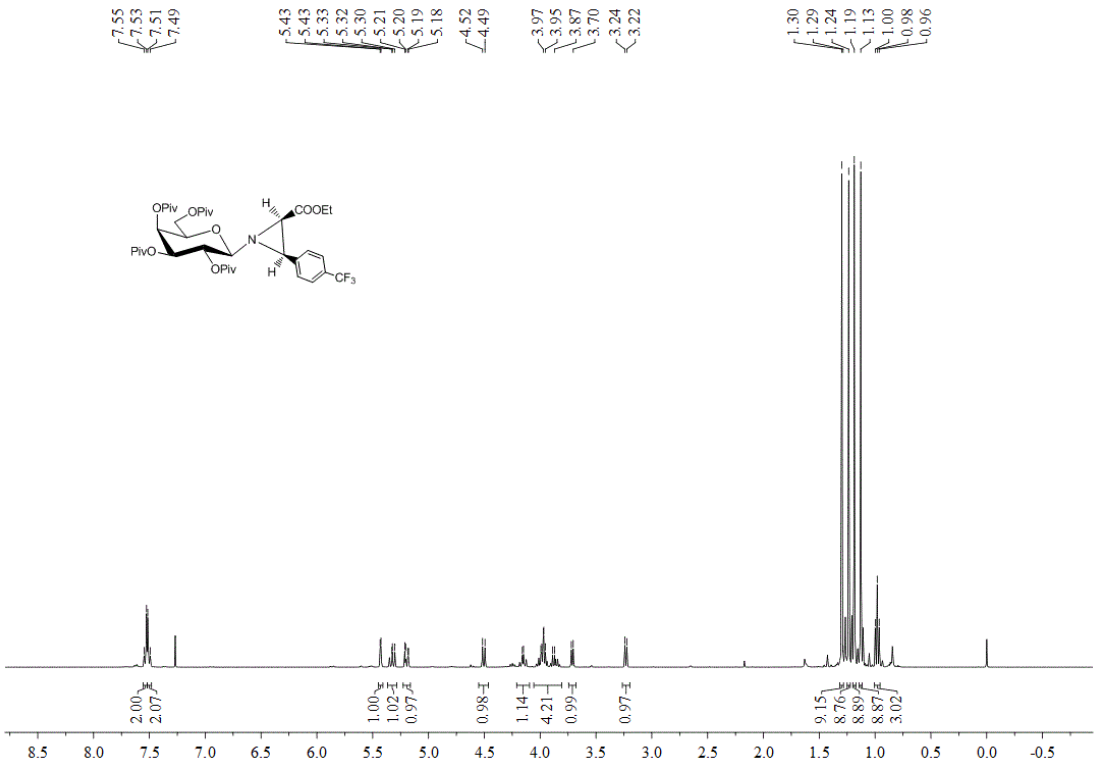
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4.49
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3.95
3.87
3.70
3.24
3.22
1.30
1.29
1.24
1.19
1.13
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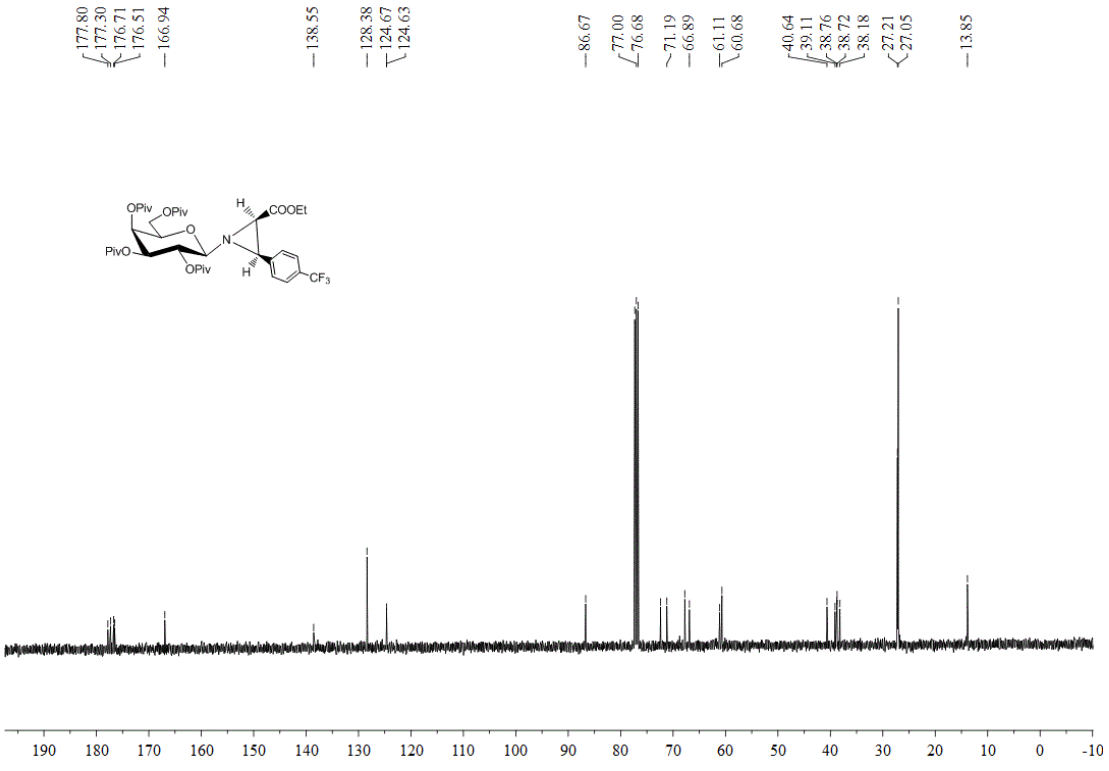
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61.11
60.68
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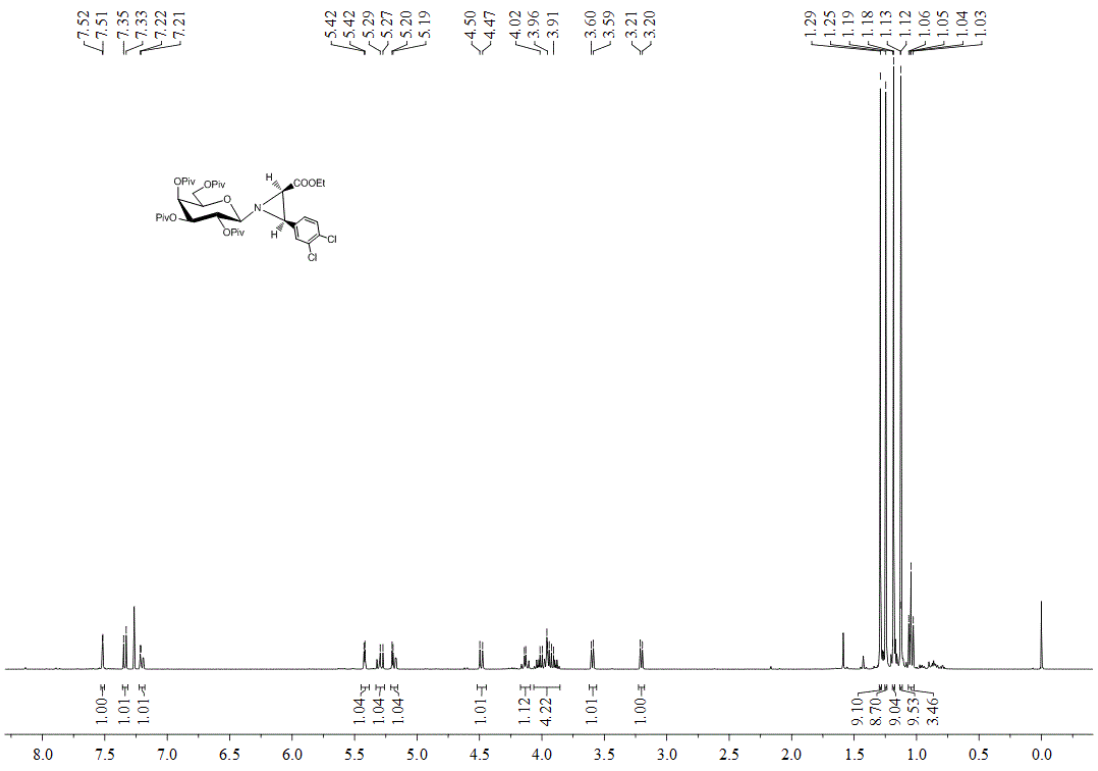
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OPiv
PivO
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COOEt
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Cl
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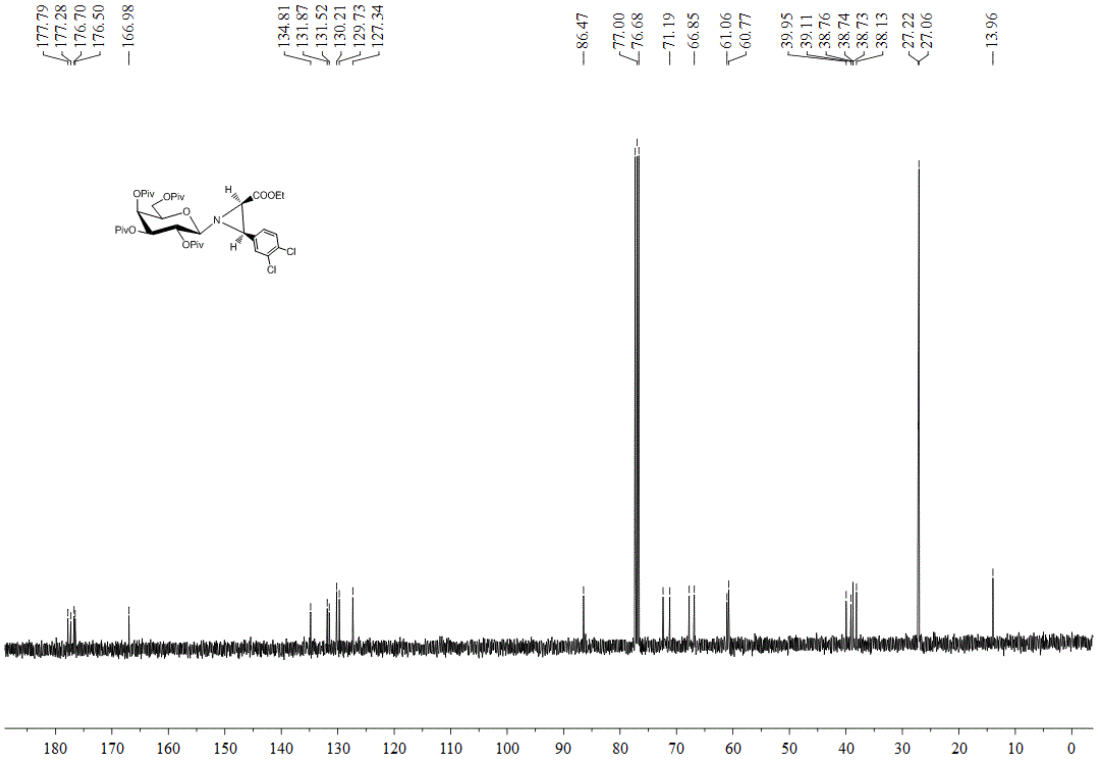
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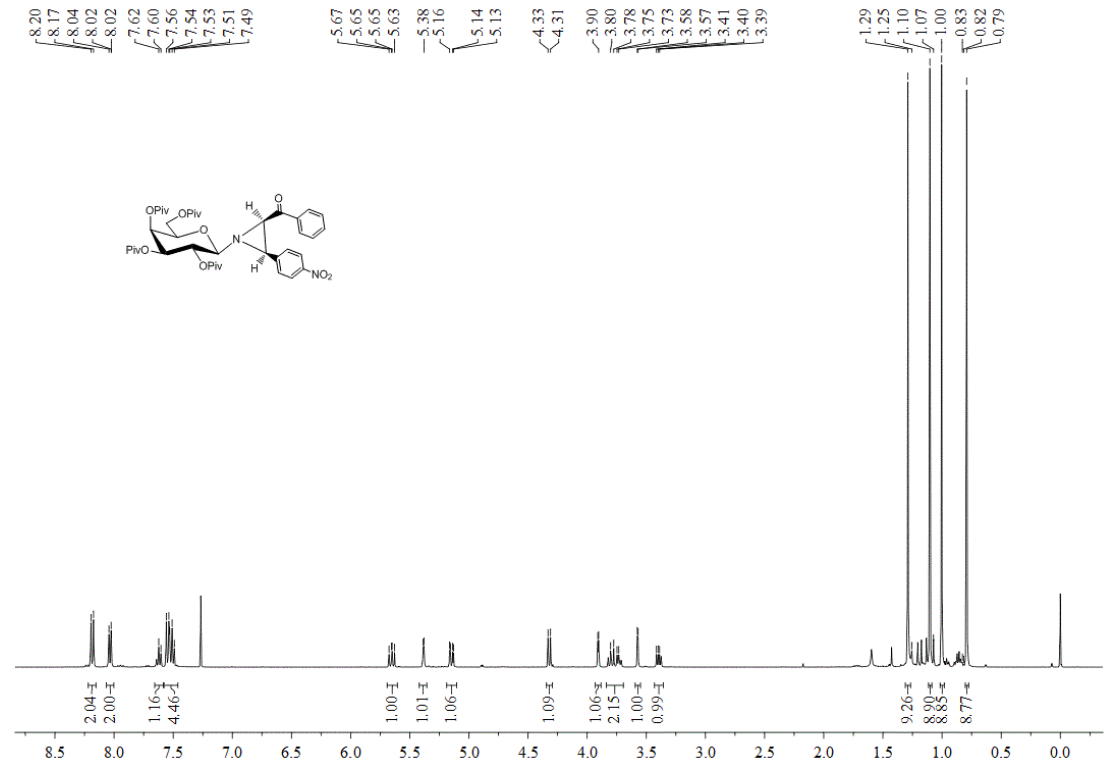
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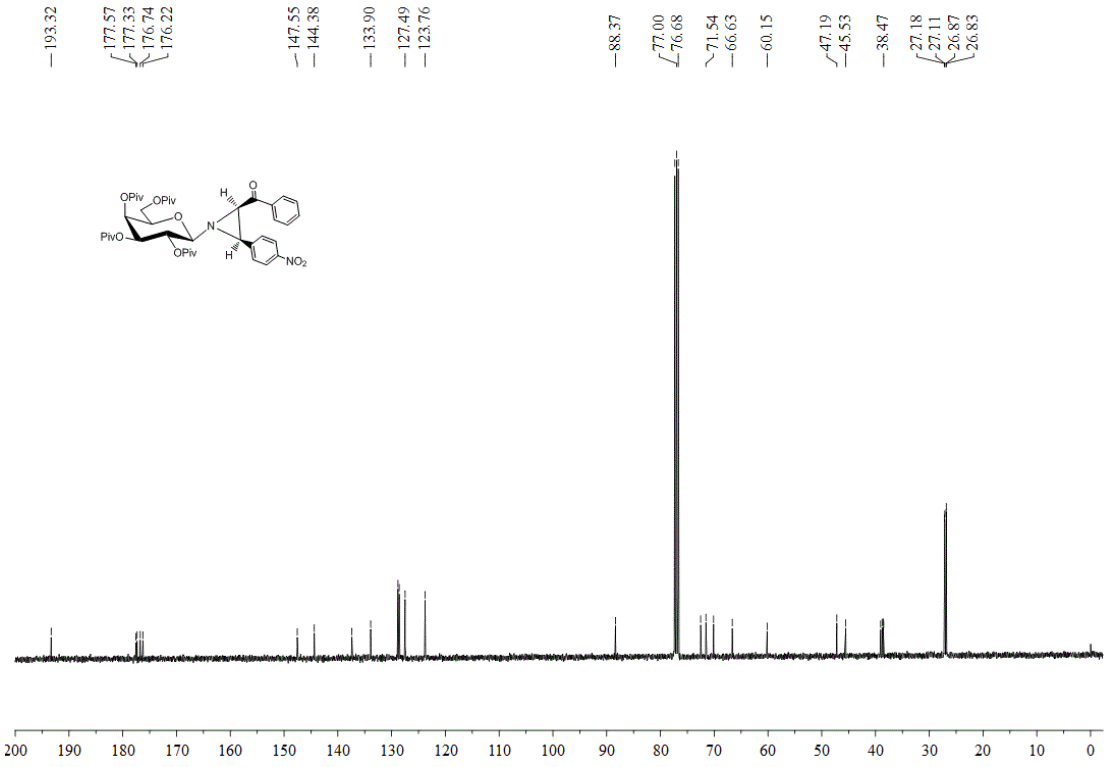
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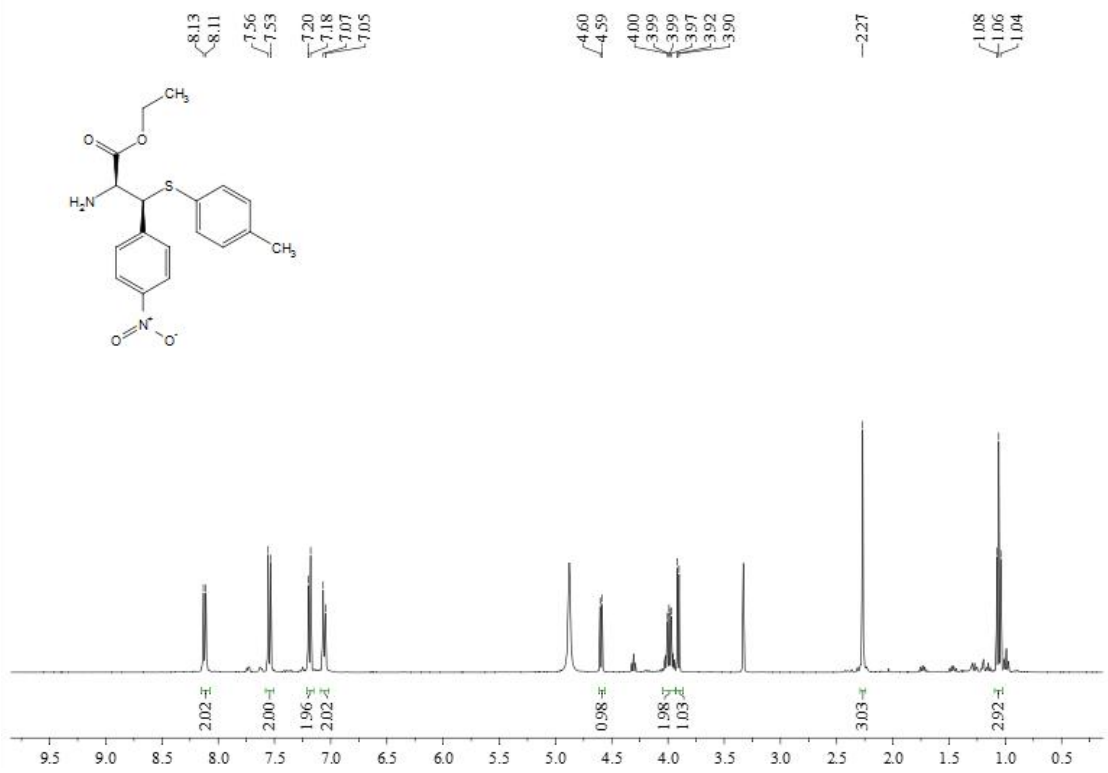
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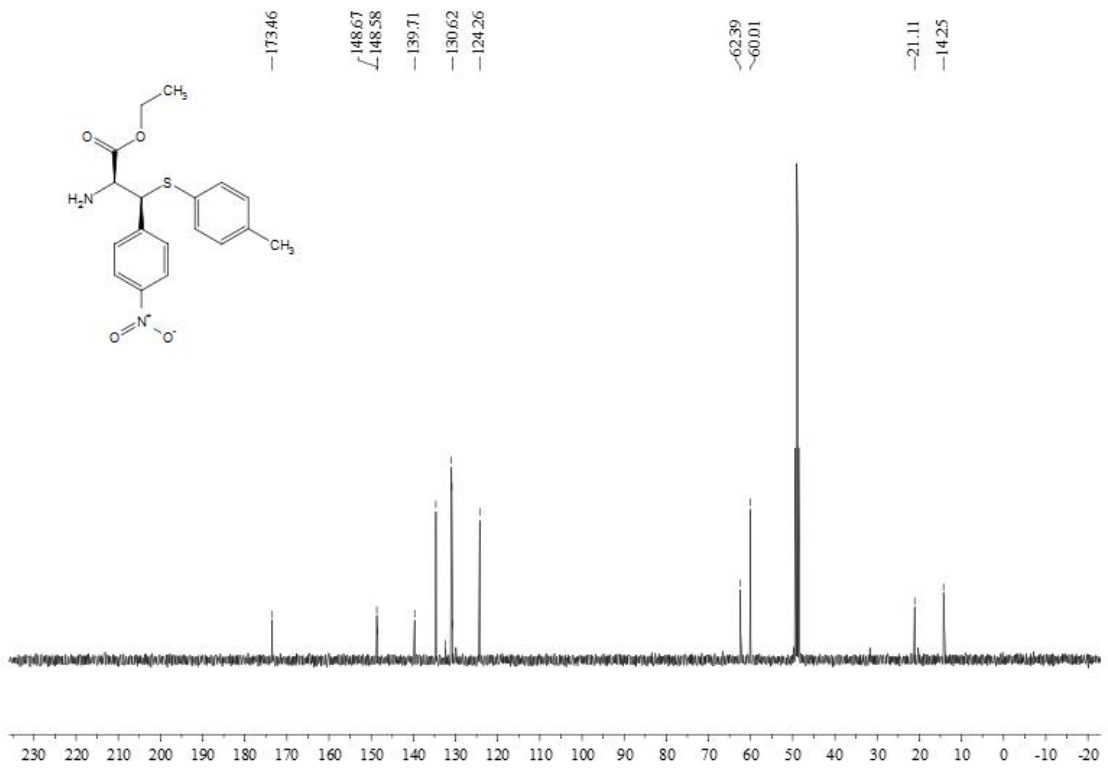
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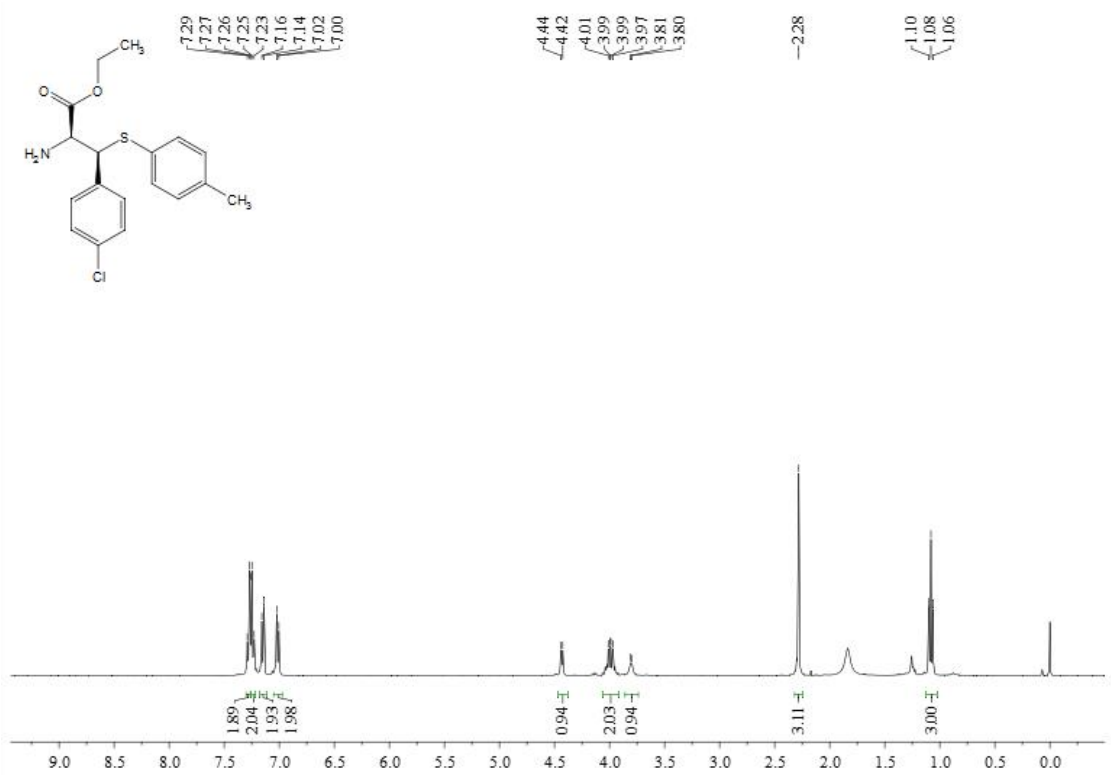
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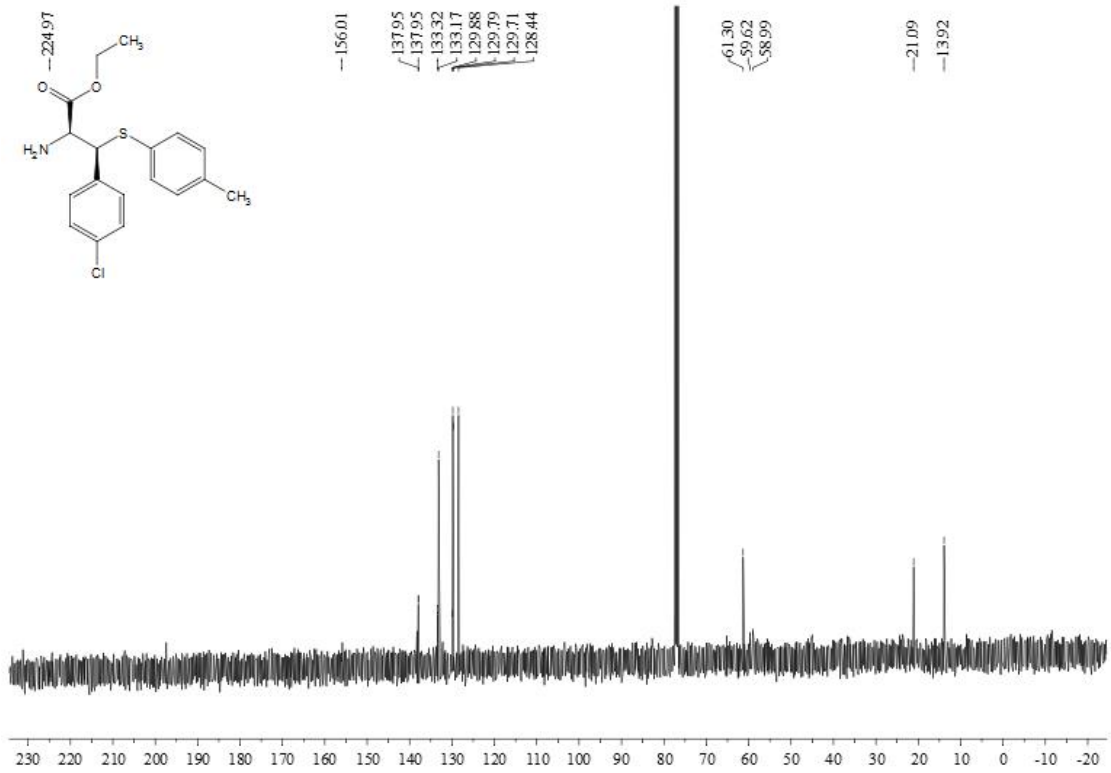
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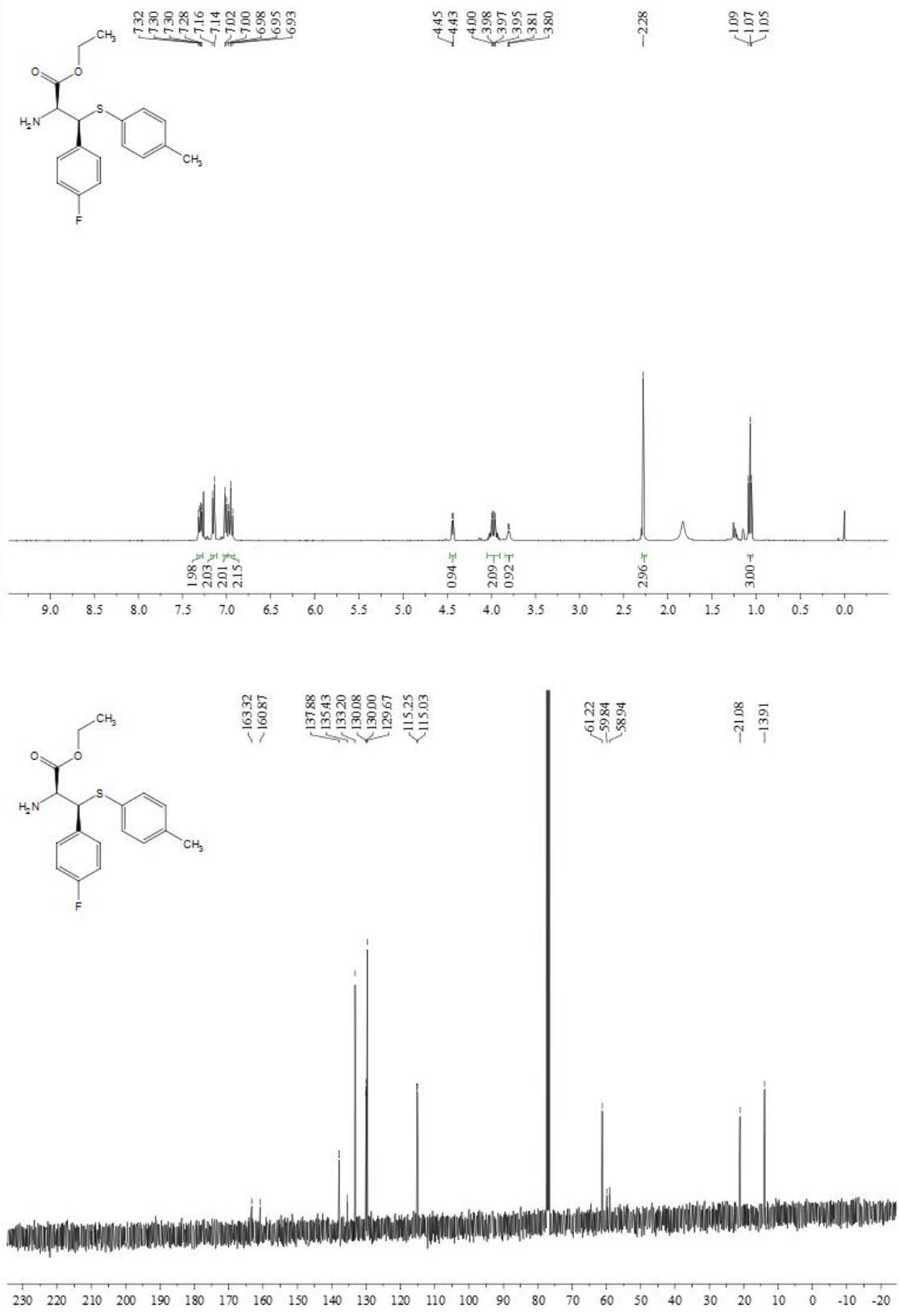
4c: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1.98
2.03
2.01
2.15
0.94
2.09
0.92
2.96
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
163.32
160.87
137.88
135.43
133.20
130.08
130.00
129.67
115.25
115.03
61.22
59.84
58.94
21.08
13.91
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

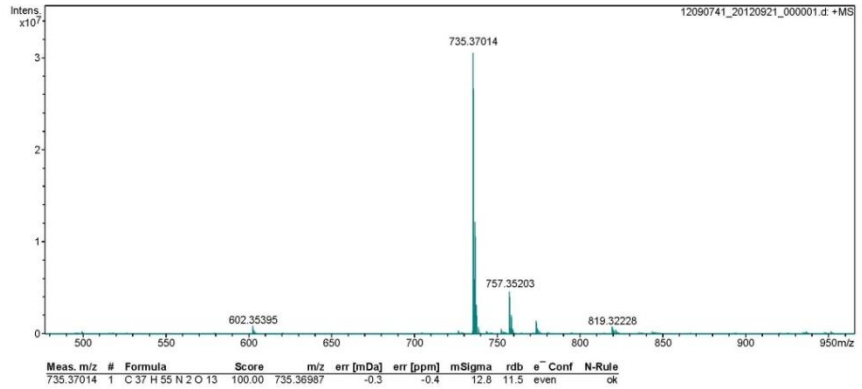
Copies of HR-ESI-MS spectra of 3 and 4

3a:

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12090741_20120921_000001.d	Acquisition Date	9/21/2012 5:48:28 PM
Sample	zss09201	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



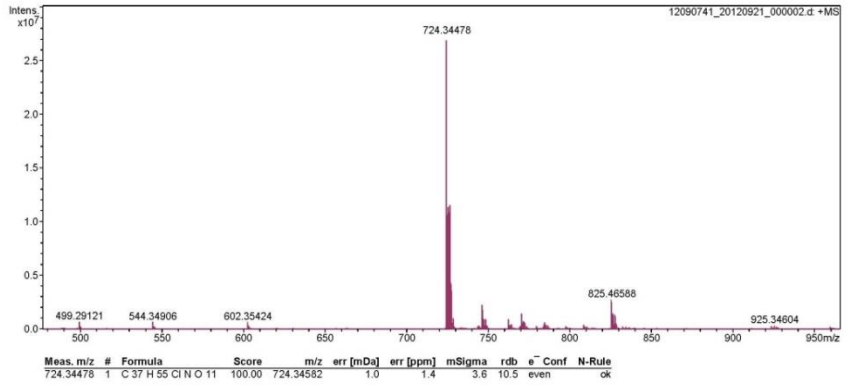
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
735.37014	1	C 37 H 55 N 2 O 13	100.00	735.36987	-0.3	-0.4	12.8	11.5	even	ok

3b:

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12090741_20120921_000002.d	Acquisition Date	9/21/2012 5:49:34 PM
Sample	zss09202	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



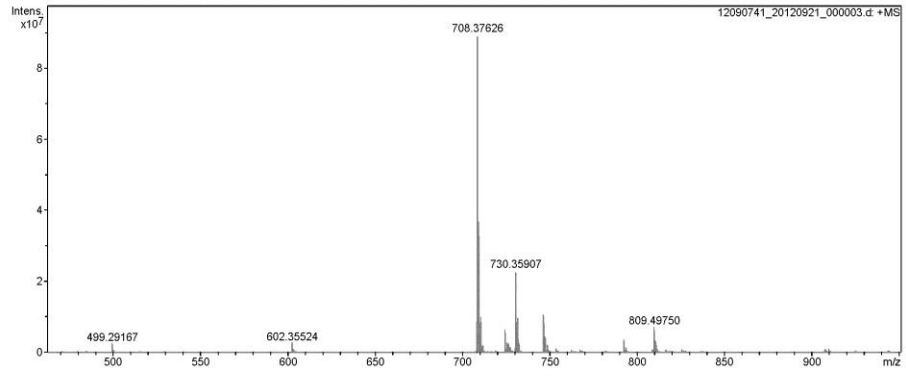
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
724.34478	1	C 37 H 55 Cl N O 11	100.00	724.34582	1.0	1.4	3.6	10.5	even	ok

3c:

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12090741_20120921_000003.d	Acquisition Date	9/21/2012 5:50:39 PM
Sample	zss09203	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



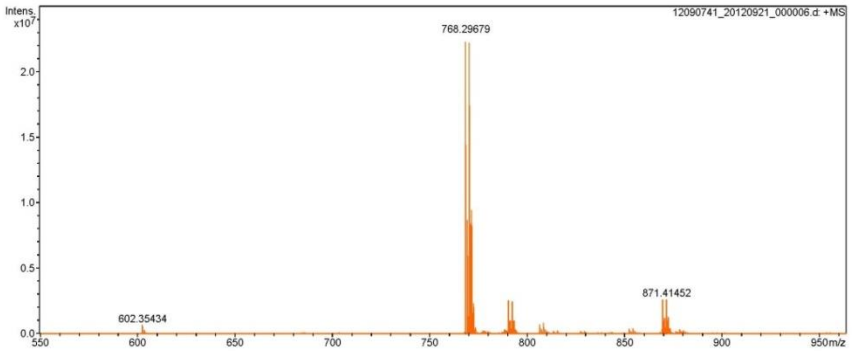
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
708.37626	1	C 37 H 55 F N O 11	100.00	708.37537	-0.9	-1.3	9.4	10.5	even	ok

3d:

Peking University Mass Spectrometry Sample Analysis Report

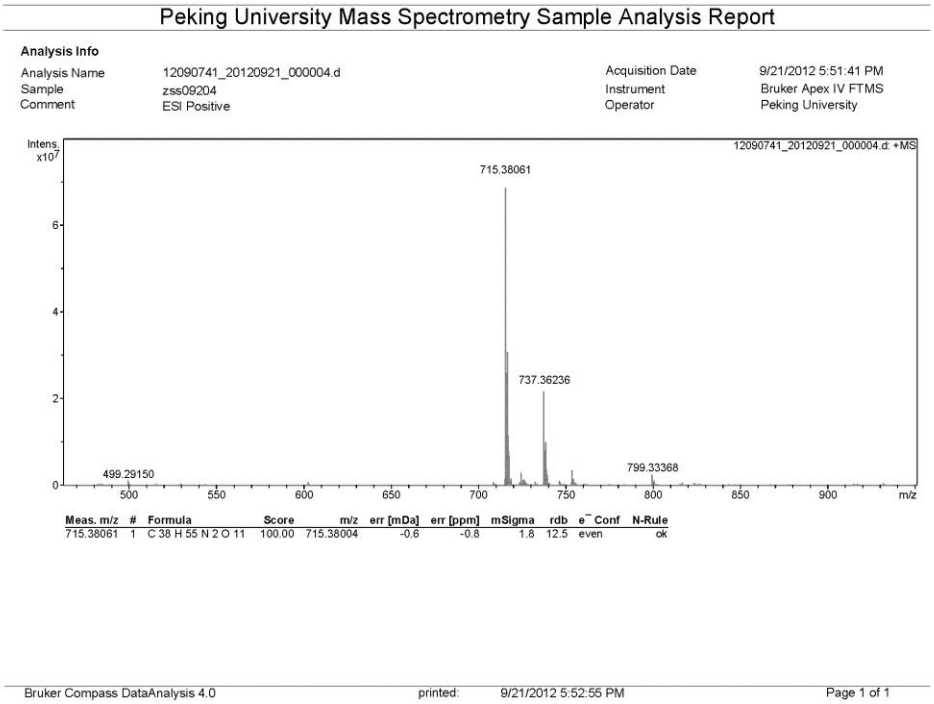
Analysis Info

Analysis Name	12090741_20120921_000006.d	Acquisition Date	9/21/2012 5:53:50 PM
Sample	zss09206	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
768.29679	1	C 37 H 55 Br N O 11	100.00	768.29530	-1.5	-1.9	32.1	10.5	even	ok

3e:



Peking University Mass Spectrometry Sample Analysis Report

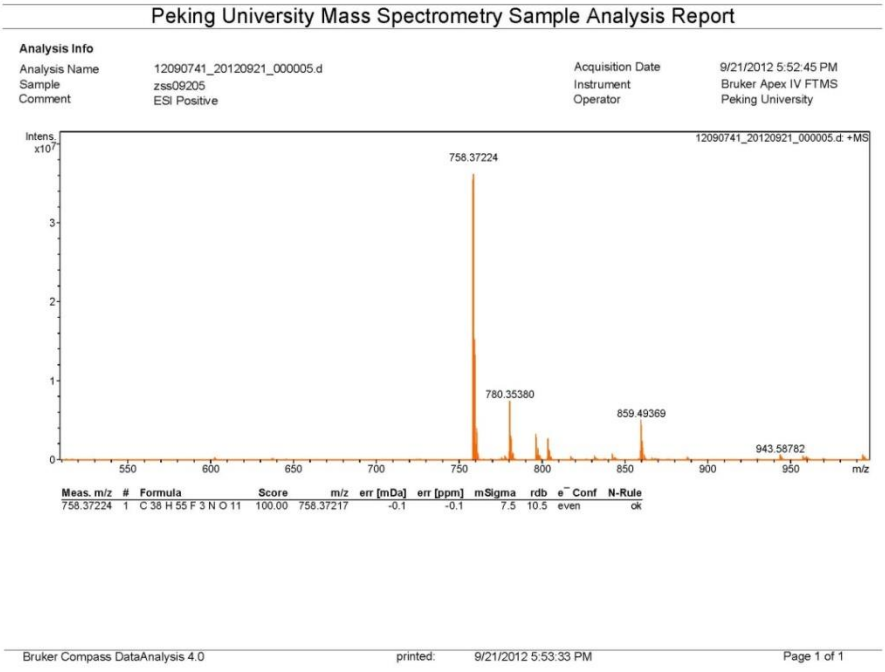
Analysis Info

Analysis Name	12090741_20120921_000004.d	Acquisition Date	9/21/2012 5:51:41 PM
Sample	zss09204	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
715.38061	1	C 38 H 55 N 2 O 11	100.00	715.38004	-0.6	-0.8	1.8	12.5	even	ok

Bruker Compass DataAnalysis 4.0 printed: 9/21/2012 5:52:55 PM Page 1 of 1

3f:



Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12090741_20120921_000005.d	Acquisition Date	9/21/2012 5:52:45 PM
Sample	zss09205	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
758.37224	1	C 38 H 55 F 3 N O 11	100.00	758.37217	-0.1	-0.1	7.5	10.5	even	ok

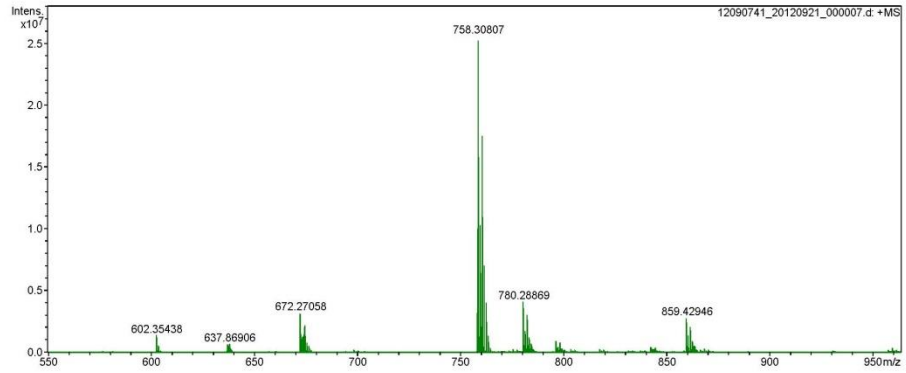
Bruker Compass DataAnalysis 4.0 printed: 9/21/2012 5:53:33 PM Page 1 of 1

3j:

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12090741_20120921_000007.d	Acquisition Date	9/21/2012 5:54:51 PM
Sample	zss09207	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



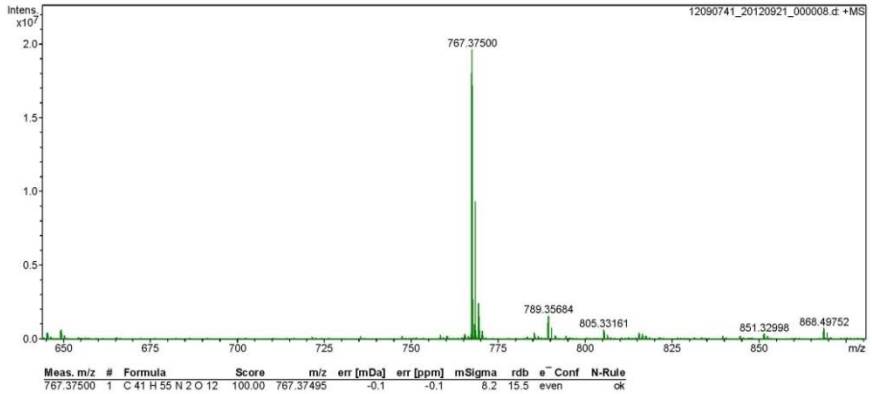
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
758.30807	1	C 37 H 54 Cl 2 N O 11	100.00	758.30684	-1.2	-1.6	17.1	10.5	even	ok

3k:

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12090741_20120921_000008.d	Acquisition Date	9/21/2012 5:55:52 PM
Sample	zss09208	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



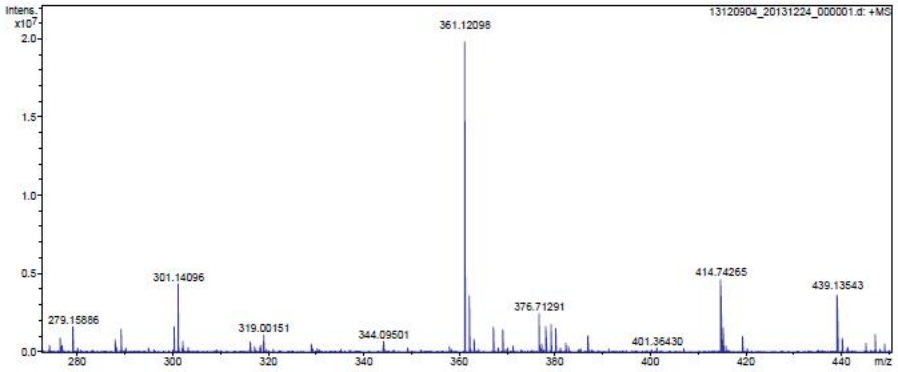
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
767.37500	1	C 41 H 55 N 2 O 12	100.00	767.37495	-0.1	-0.1	8.2	15.5	even	ok

4a:

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	13120904_20131224_000001.d	Acquisition Date	12/24/2013 1:52:53 PM
Sample	zyzpno2	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



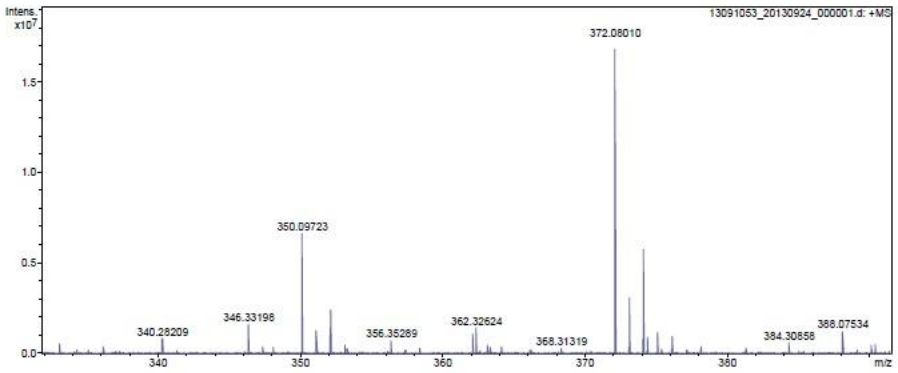
Meas. m/z	I	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
361.12098	20465658	C 18 H 21 N 2 O 4 S	361.12165	0.7	1.9	23.2	9.5	even	ok

4b:

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	13091053_20130924_000001.d	Acquisition Date	9/24/2013 3:17:16 PM
Sample	ZYZ	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



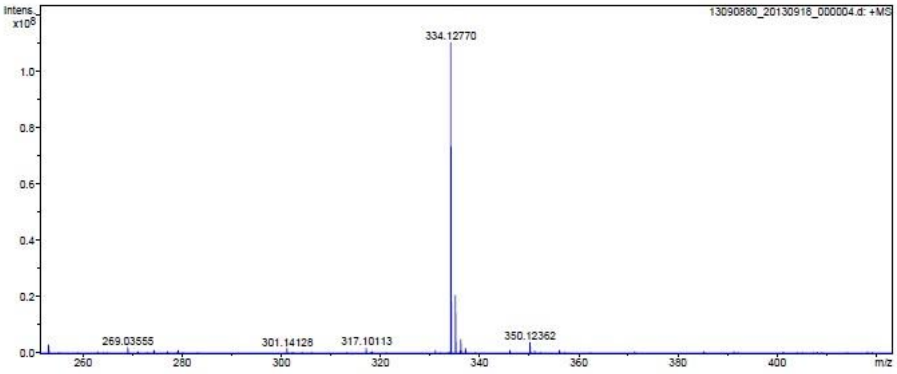
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
350.09723	1	C 18 H 21 Cl N O 2 S	100.00	350.09760	0.4	1.1	13.3	8.5	even	ok
372.08010	1	C 18 H 20 Cl N Na O 2 S	100.00	372.07955	-0.6	-1.5	24.5	8.5	even	ok

4c:

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	13090880_20130918_000004.d	Acquisition Date	9/18/2013 5:01:13 PM
Sample	zyz2	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
334.12770	1	C 18 H 21 F N O 2 S	100.00	334.12715	-0.5	-1.6	15.9	8.5	even	ok

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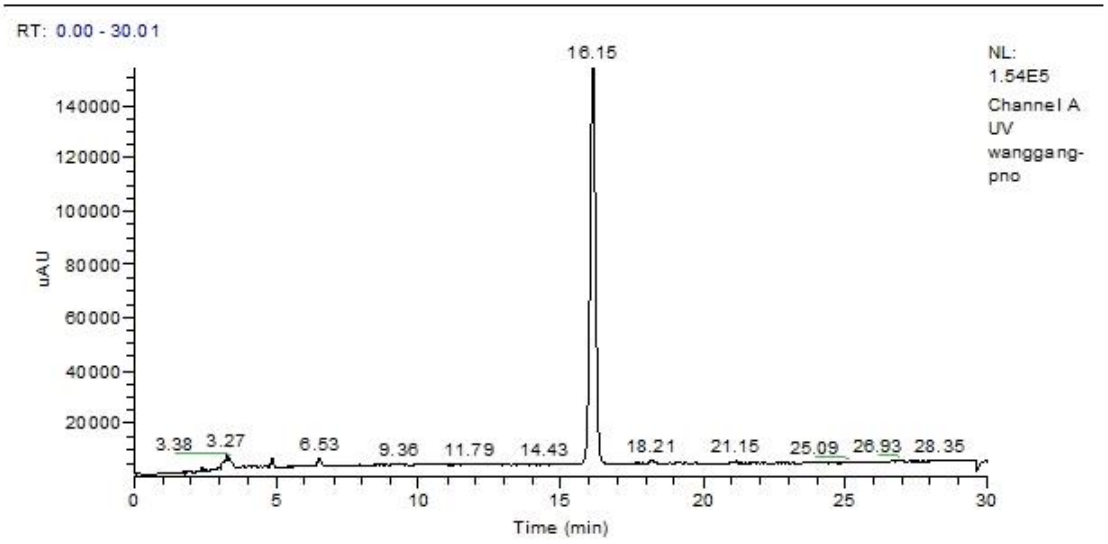
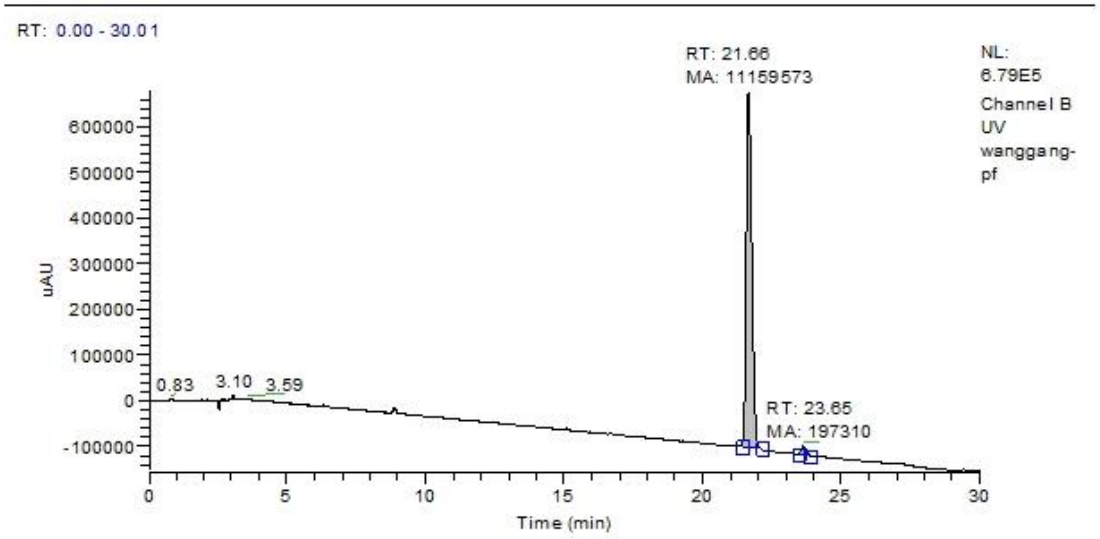
Copies of chiral HPLC data of 3 and 4

3a:



3b:



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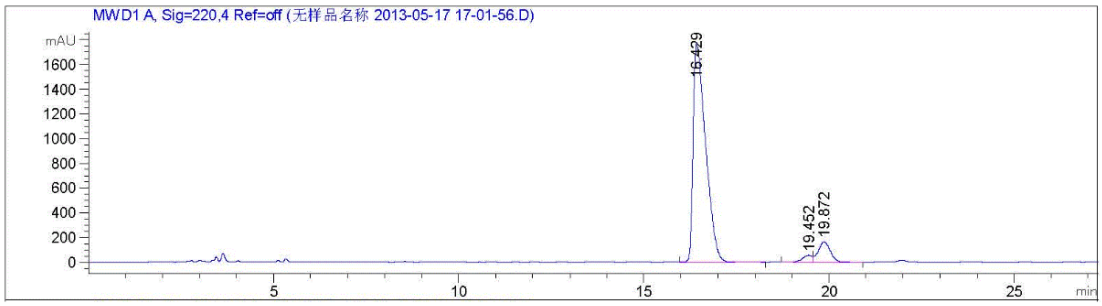

信号 1: MWD1 A, Sig=220,4 Ref=off

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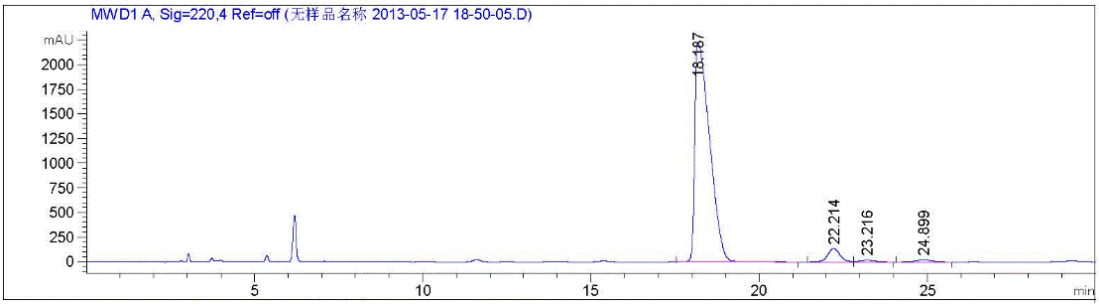
1	16.429	VB	0.3511	4.12330e4	1774.35815	89.5958
2	19.452	BV	0.2846	1069.91467	56.07209	2.3248
3	19.872	VB	0.3428	3718.21240	165.05069	8.0794

总量 : 4.60211e4 1995.48093

3d:

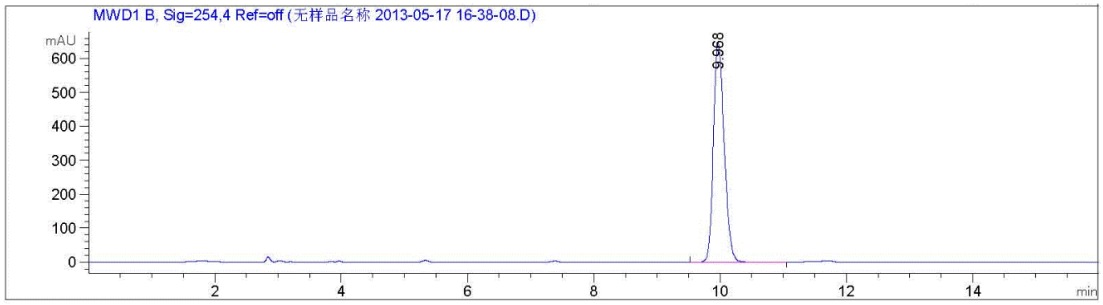


信号 1: MWD1 A, Sig=220,4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.187	BB	0.4762	6.79308e4	2225.08398	94.0606
2	22.214	BV	0.3758	3267.39575	134.34055	4.5242
3	23.216	VB	0.3876	419.78641	16.68236	0.5813
4	24.899	BB	0.4090	602.27289	22.73775	0.8339

总量 : 7.22203e4 2398.84464

3e:



信号 2: MWD1 B, Sig=254,4 Ref=off

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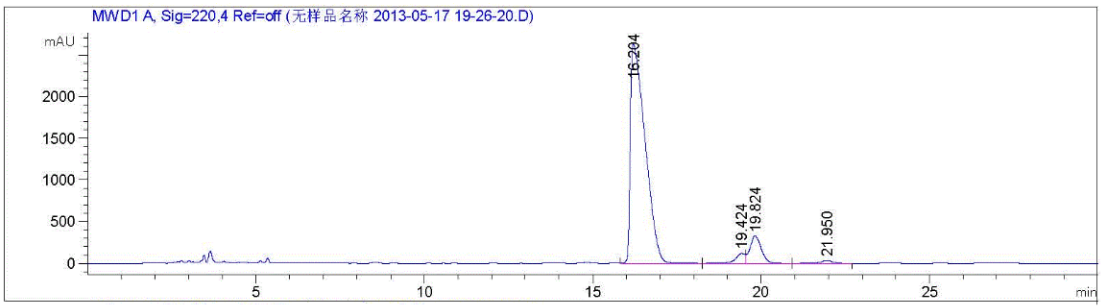
1	9.968	BB	0.1841	7641.28223	645.74554	100.0000
总量：				7641.28223	645.74554	

3f:



信号 1: MWD1 A, Sig=220,4 Ref=off

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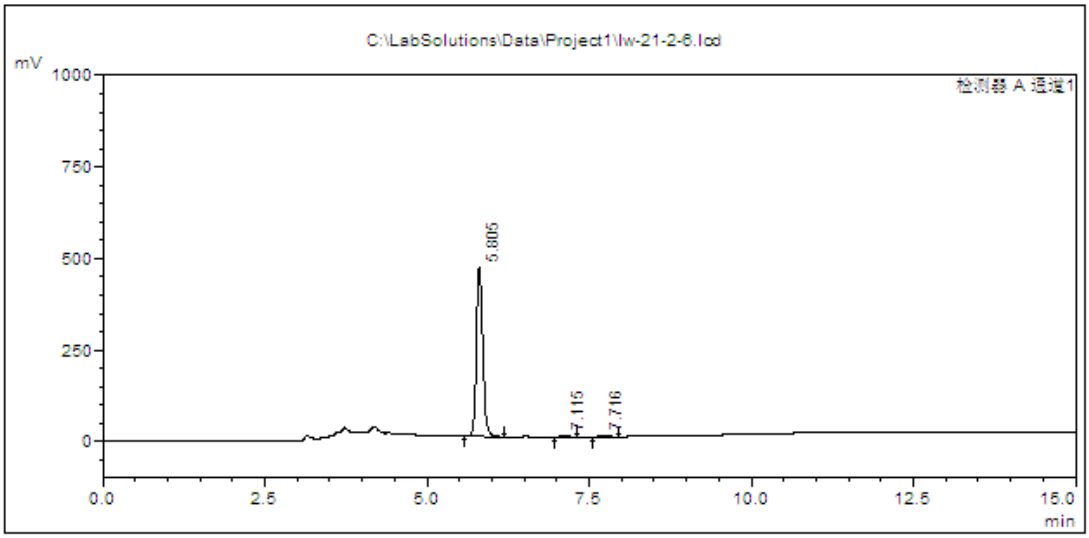
1	16.204	VB	0.4205	7.94137e4	2628.37769	88.3491
2	19.424	BV	0.2770	2203.21704	117.37755	2.4511
3	19.824	VB	0.3533	7554.48926	324.88876	8.4045
4	21.950	BB	0.3824	714.80963	28.71903	0.7952
总量：				8.98862e4	3099.36302	

3j:

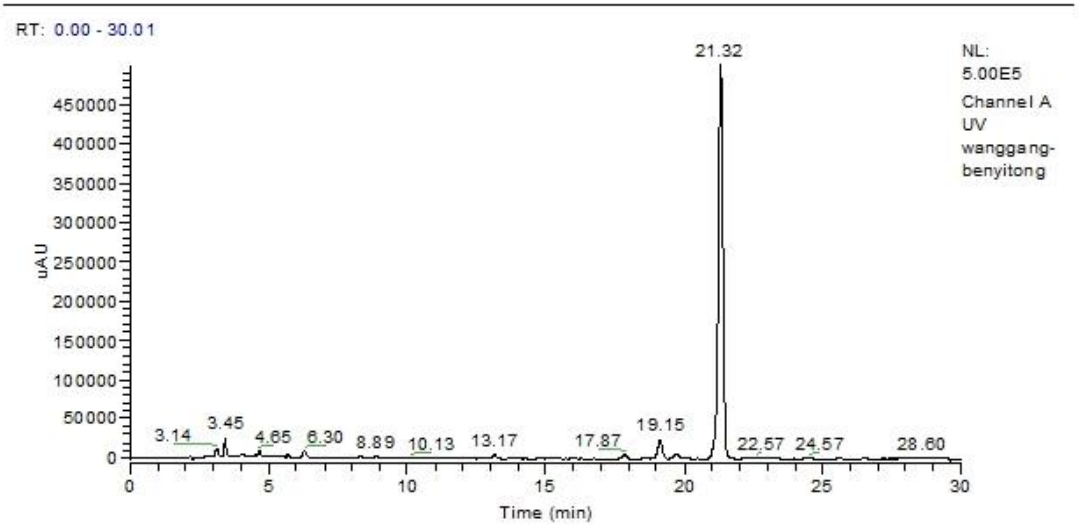


峰表

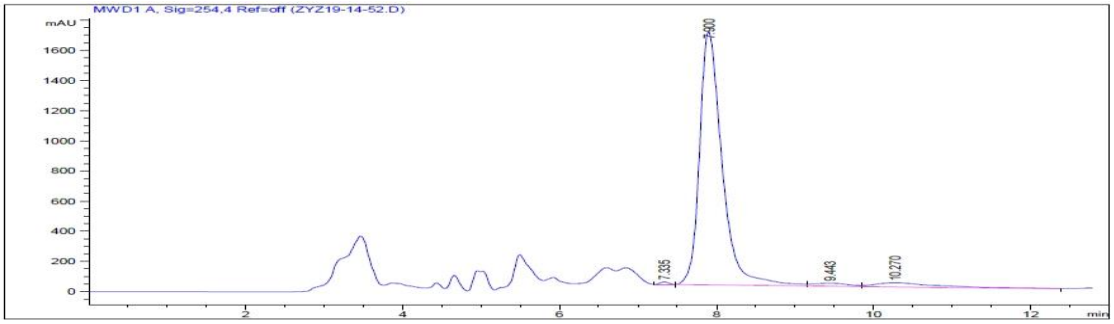
检测器 A Ch1 220nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	5.805	3128591	463283	98.380	98.698
2	7.115	24473	2978	0.770	0.634
3	7.716	27058	3133	0.851	0.667
总计		3180122	469393	100.000	100.000

3k:



4a:



信号 1: MWD1 A, Sig=254,4 Ref=off

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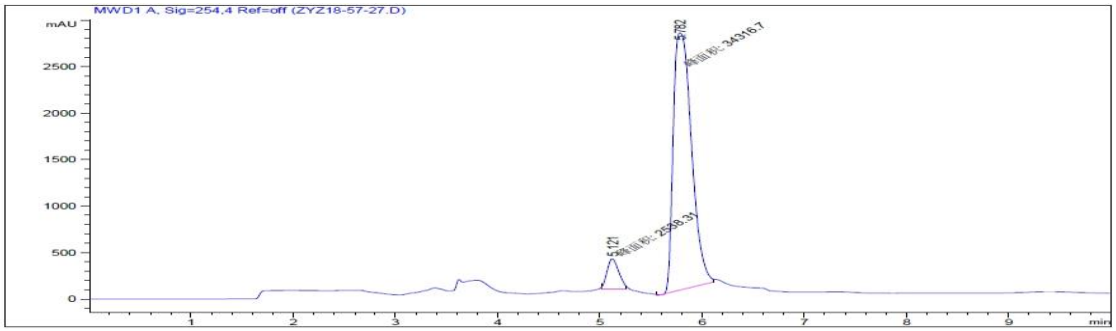
1	7.335	BB	0.1237	124.83826	16.60329	0.3497
2	7.900	BV	0.3005	3.34783e4	1679.68140	93.7897
3	9.443	VV	0.4392	605.48401	20.00107	1.6963
4	10.270	VB	0.7278	1486.44800	28.07254	4.1643
总量 :				3.56950e4	1744.35830	

4b:



信号 1: MWD1 A, Sig=254,4 Ref=off

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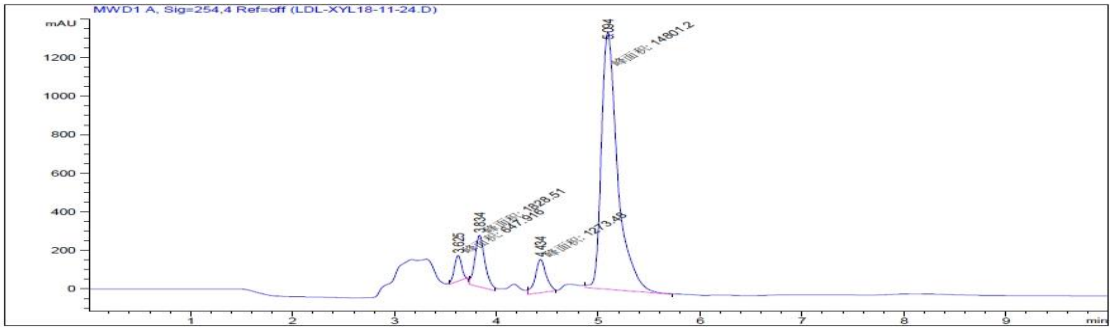
1	5.121	MM	0.1304	2538.30786	324.31229	6.8873
2	5.782	MM	0.2066	3.43167e4	2767.93555	93.1127
总量 :				3.68550e4	3092.24783	

4c:



信号 1: MWD1 A, Sig=254,4 Ref=off

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1	3.625	MM	0.0806	647.91589	133.94518	3.4926
2	3.834	MM	0.1140	1828.50806	267.26379	9.8566
3	4.434	MM	0.1221	1273.48450	173.87038	6.8647
4	5.094	MM	0.1849	1.48012e4	1334.19653	79.7861
总量 :				1.85511e4	1909.27588	